ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF V-SHAPED GRAFT COPOLYMERS VIA TRIPLE CLICK REACTIONS

M.Sc. THESIS

Bengü ÖZSOY

Department of Chemistry

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÜÇLÜ KLİK REAKSİYONLARI İLE V-ŞEKİLLİ AŞI KOPOLİMERLERİ SENTEZİ

YÜKSEK LİSANS TEZİ

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HAZİRAN 2012

Bengü ÖZSOY, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 509101091, successfully defended the **thesis** entitled "**SYNTHESIS OF V-SHAPED GRAFT COPOLYMERS VIA TRIPLE CLICK REACTIONS**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 3 May 2012
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To my family,

FOREWORD

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May 2012

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ABBREVIATIONS

ATRP : Atom Transfer Radical Polymerization
ε-CL : ε-caprolactone
CMS : 4-Chloro methyl styrene
CuAAC : Copper catalyzed azide-alkyne cycloaddition
$CDCl_3$: Deuterated chloroform
CH_2Cl_2 : Dichloromethane
DSC : Differential Scanning Calorimetry
DMF : *N*,*N*-Dimehthylformamide
EtOAc : Ethyl acetate
FT-IR : Fourier Transform Infrared Spectrophotometer
GPC : Gel Permeation Chromatography
^{1}H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
MeOH : Methanol
MWD : Molecular Weight Distribution
NMP : Nitroxide Mediated Polymerization
NRC : Nitroxide Radical Coupling
PMDETA : *N, N, N',N'', N''*-Pentamethyldiethylenetriamine
PCL : Poly(ε-caprolactone)
PEG : Poly(ethylene glycol)
PS : Poly(styrene)
RAFT : Reversible Addition Fragmentation Chain Transfer
ROMP : Ring-Opening Metathesis Polymerization
ROP : Ring-Opening Polymerization
St : Styrene
THF : Tetrahydrofuran
TEMPO : 2,2,6,6-Tetramethylpiperidine-*N*-oxyl
TEA : Triethylamine
TD-GPC : Triple Detector-Gel Permeation Chromatography

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SYNTHESIS OF V-SHAPED GRAFT COPOLYMERS VIA TRIPLE CLICK REACTIONS

SUMMARY

Polymers with complex architecture play key roles in understanding structure property relationships and exploring new materials. The construction of complex macromolecules exhibiting a precise architecture, size, shape, and functionality is a challenging domain with rapidly growing interest. Complex macromolecules have been prepared in the search for polymers with developed mechanical and physical properties. V-shaped polymers, a class of complex macromolecular structures difficult to synthesize graft polymer have been recently obtained by the use of click reactions. In the literature, there are a lot of varieties of V-shaped graft copolymers of are synthesized via a combination nitroxide mediated radical polymerization (NMP), and anionic polymerization.

The ionic polymerizations (anionic or cationic) were the only living systems available until last decade. Contolling molecular weight, well-defined chain ends, and low polydispersity are the most usefull advantages of controlling/living polymerization systems. Atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), and reversible addition-fragmentation chain transfer polymerization (RAFT) are most widely used methods for C/LRP.

Nowadays, alternative routes such as Diels-Alder (DA) and the copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) reactions which can be classified under the term “click chemistry” have emerged as a powerful tool for the preperation of graft polymers. In addition, nitroxide radical coupling reactions (NRC) reaction is considered as a potential click reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies.

Meanwhile, the development of the click reactions particularly, copper (I) catalyzed azide-alkyne cycloaddition (CuAAC) and Diels–Alder (DA) reactions have provided new synthetic pathways for the preparation of V-shaped copolymers. From this point of view, in this thesis, we describe the synthesis of graft copolymers using subsequently ROMP, DA and NRC reactions.

For this purpose, in this study; firstly, maleimide terminated PEG is synthesized via esterification reaction. Poly(ethylene glycol)methyl ether (Me-PEG), DCC and DMAP are used. Secondly, a trifunctional core was designed as containing anthracene, bromide and alkyne functionalities. Compounds, succinic acid mono-anthracen-9-ylmethyl-ester and Propargyl-3-[(2-bromo-2-methylpropanoyl)oxy-2-(hyroxymethyl)-2-methylpropanoate are used for Anthracen-9-ylmetyl-2((2-bromo-2-methylpropanoxy)methyl)2-methyl-3-oxo-3-(prop-2-ynyloxy)-propylsuccinate. α-alkyne-α-bromide-terminated PEG is synthesized via Diels Alder reactions between furan-protected maleimide-terminated poly(ethylene glycol) (PEG-MI) and 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid. Two different backbone copolymers,

Poly(ONB-butyl)$_{15}$-*b*-Poly(ONB-Azide)$_5$ copolymer and copolymers of St and 4-chloromethylstyrene P(S-*co*-CMS) are synthesized. The first backbone, P(S-*co*-CMS) copolymer was prepared via NMP of St and CMS at 125 ^{o}C with a feed ratio of 10 mol % CMS. The second backbone, (ONB-butyl)$_{15}$-*b*-Poly(ONB-Azide)$_5$ copolymer is prepared via ROMP of monomers 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione and 4-(2-{[(3-acetyl-7-oxabicyclo [2.2.1]hept-yl)carbonyl]amino}ethoxy)-4-oxobutanoic acid. Finally, V-shaped graft copolymers are synthesized by combination of C/LRP methods with click reactions which involve CuAAC, NRC and Diels-Alder.

ÜÇLÜ KLİK REAKSİYONLARI İLE V-ŞEKİLLİ KOPOLİMERLER SENTEZİ

ÖZET

Yaşayan iyonik polimerizasyon yöntemi, lineer olmayan yapıdaki polimer sentezleri için kullanılan polimerizasyon tekniklerinden en önemlisiydi. Son yıllarda, kompleks makromoleküllerin sentezinde kontrollü/yaşayan polimerizasyon tekniklerinin kullanılması, yaşayan iyonik polimerizasyon yöntemiyle mukayese edildiğinde deneysel koşullara daha fazla toleranslı olması ve çok çeşitli monomerlere uygulanabilir olması nedeniyle hızlı bir şekilde arttı.

Bu polimerizasyon teknikleri, aşı, star ve dallı yapılı polimerlerin sentezi için kullanılabilir. Kontrollü kompozisyon ve yapılarda iyi tanımlanmış makromoleküllerin sentezi polimer biliminde yeni bir alan açan iyonik polimerizasyon yöntemlerinin gelişimine kadar kimyagerler için sorun olmuştu. Ancak, iyonik polimerizasyon araştırmalarının gelişimi zorlu işlem koşulları; yüksek saflık ve çeşitli fonksiyonel monomerlerle uyumsuzluk söz konusu olduğundan bazı ciddi engeller ile karşılaşmaktadır. Serbest radikal polimerizasyonu safsızlıklara daha toleranslıdır ve çok çeşitli vinil monomerlerinin polimerleştirilmesi yeteneğine sahiptir fakat en büyük dezavantajı iyonik polimerizasyondaki gibi polimer yapı ve fonksiyonalite kontrolünün aynı derecede mümkün olmamasıdır.

Kontrollü radikal polimerizasyon teknikleri; Atom transfer radikal polimerizasyonu (ATRP), nitroksit ortamlı radikal polimerizasyonu (NMP) ve tersinir eklenme-parçalanma zincir transferi polimerizasyonu (RAFT)' dır.

Kontrollü radikal polimerizasyonu molekül ağırlığının polimer dönüşümüyle doğrusal bağıntı içinde olması, dolayısıyla istenilen molekül ağırlığının elde edilmesi, monodisperse yakın dar bir molekül ağırlığı dağılımı elde edilmesi, zincir sonunda fonksiyonel gruplara sahip polimerler elde edilmesi (*telekelik polimerler*), ve polimer moleküler mimari yapısının kontrol edilmesi (*blok kopolimerler*) gibi avantajlara sahiptir.

Bir nevi katılma polimerizasyon mekanizmasına sahip olan yaşayan polimerizasyon reaksiyonlarında büyüyen polimer zincirinin sonlanma adımı ortadan kaldırılmıştır. Daha doğrusu, sonlanma ve başlama basamakları dış etmenlerle kontrollü bir şekilde yapılır. Bu sayede polimerin molekül ağırlığı ve polimer zincirlerinin zincir sonu grupları kontrol edilir. Zincir sonuna eklenebilecek farklı fonksiyonellikte gruplar ile polimerin fiziksel özellikleri uyumlaşabilir.

Sonlanma ve zincir transferi reaksiyonlarının olmadığı yaşayan polimerizasyon mekanizmalarında polimer zincirinin büyüme hızı (hemen hemen) sabittir ve reaksiyon sonunda elde edilen polimer moleküllerinin zincir büyüklükleri birbirine çok yakındır; yani monodisperse yakın molekül ağırlığı dağılımı vardır.

Genel olarak serbest radikal polimerizasyonunda polimer zincirleri ilk adımlarda hızla büyüdükleri halde , kontrollü radikal polimerizasyonda polimer zincirlerinin büyümesi doğrusal bir yol izler.

Bu polimerizasyon teknikleri aşı kopolimerleri sentezlenmesinde sıklıkla kullanılmaktadır. Aşı kopolimerlerin birçok çeşidi vardır. Bunlar, klasik aşı kopolimerler, lineer bölümlerden oluşan blok kopolimerler, yıldız aşı, blok aşı ve V-şekilli aşı kopolimerlerdir.

Aşı polimerler sahip olduğu lineer olmayan yapısı, farklı bileşimi ve topolojisi nedeniyle önemli bir ilgiye sahiptir. Dallı yapılarından dolayı genellikle düşük vizkozite değerlerine sahiptir ve bu durumda polimerin işlenme koşullarını kolaylaştırır. Ayrıca, aşı polimerler lineer polimerlere kıyasla daha iyi fiziksel ve kimyasal özelliklere sahiptirler.

Klik kimyası Sharpless ve çalışma arkadaşları tarafından ortaya çıkarılmıştır. Klik kimyası yüksek verimle ürün eldesi, fonksiyonel gruplara karşı olan tolerans ve seçicilik önemli özellikler arasındadır. Günümüzde, "klik kimyası" terimi altında sınıflandırılan Diels-Alder (DA) ve bakır katalizli azid-alkin siklokatılma (CuAAC) tepkimeleri blok ve yıldız polimerlerin eldelerinde güçlü bir alternatif yöntem olarak ortaya çıkmıştır. Buna ek olarak , nitroksit radikal birleşme reaksiyonları (NRC) farklı topolojileri iyi tanımlanmış polimerlerin sentezi, yüksek verimlilik nedeniyle potansiyel bir click reaksiyonu olarak kabul edilir.Bu noktadan hareketle bu tezde ROMP, DA ve NRC reaksiyonlarının birlikte kullanılmasıyla aşı kopolimerlerinin sentezi tanımlanmıştır.

Bu tez çalışmasında, kontrollü/yaşayan polimerizasyon teknikleri ile Klik kimyası yöntemleri kullanılmış ve sonuç ürünleri olarak V-şekilli aşı kopolimerleri sentezlenmiştir. Klik kimyasının yanında yaşayan/kontrollü polimerizasyon tekniklerinden olan NMP ve ROMP yöntemleri ile V-şekilli aşı kopolimerinin iskeletini oluşturacak olan iki adet kopolimer sentezlenmiştir. Bu kopolimerler, PEG-çekirdek adını verdiğimiz maddemiz , üçüncü ve dördüncü bölümlerde ayrıntılı anlatılacaktır,ve üçüncü maddemiz PCL-TEMPO ile aynı anda gerçekleşen klik reaksiyonları ile V-şekilli aşı kopolimerlerini oluşturdular.

Öncelikle, çekirdek adı verilen üç fonksiyona sahip madde sentezlenmiştir. Çekirdeğin sentezlenmesinde birçok polimerizasyon yöntemi kullanılmıştır. Çekirdek sentezi için uygulanan prosedürde, maleik anhidrit, toluen içerisinde çözülmüş, furan eklenmiş ve 4,10-dioxatrisiklo[5.2.1.02,6]dec-8-ene-3,5-dion elde edilmiştir. 4,10-dioxatrisiklo[5.2.1.02,6]dec-8-ene-3,5-dion maddesi alkol haline çevrilerek 4-(2-hidroksietil)-10-oxa-4-azatrisiklo[5.2.1.02,6]dec-8-ene-3,5-dion maddesine çevrilmiştir. 4-(2-hidroksietil)-10-oxa-4-azatrisiklo[5.2.1.02,6]dec-8-ene-3,5-dion maddesi trietilamin, süksinik anhihrit ve DMAP eldesi ile asit formuna çevrilerek 4-(2-{[(3-acetil-7-oxabisiklo[2.2.1]hept-il)carbonil]amino} ethoxy)-4-oxobutanoik asit elde edilmiştir. Poli(etilen glikol) metil eter (Me-PEG), ile 4-(2-{[(3-acetil-7-oxabisiklo[2.2.1]hept-il)carbonil]amino} ethoxy)-4-oxobutanoik asit reaksiyonu sonucu furan-korumalı maleimid sonlu (PEG-MI) elde edilmiştir.

9-antresan methanol, trietilamin ve DMAP maddeleri reaksiyonu sonucu süksinik asit mono-antrasen-9-ylmetil-ester elde edilmiştir. Çekirdek, süksinik asit mono-antrasen-9-ylmetil-ester ve propargyl-3-[(2-bromo-2-metilpropanoyl)oxy-2-(hidroksimetil)-2-metilpropanoate maddeleri arasındaki reaksiyon sonucu sentezlenmiştir. Sentezlenen üç fonksiyonu bulunan çekirdek, ile PEG-MI arasında

Diels-Alder reaksiyonu sonucunda α-alkin-α-brom uçlu PEG-çekirdek elde edilmiştir.

İkinci aşama olarak, sonuç polimerlerinin iskeletini oluşturacak olan kopolimerler sentezlenmiştir. Bunlardan birincisi, stiren ve 4-klorometilstiren arasında NMP yöntemi ile 125°C' de sentezlenen, stiren-klorometilstiren kopolimeridir, P(S-*co*-CMS). Bu kopolimerdeki klor fonksiyonları ikinci aşama olarak sodyum azid eklenerek 24 saat süren bir reaksiyon sonucu, azide dönüştürülmüştür ve polistiren azid, P(St_{48}-$Azid_5$) sentezlenmiştir. Klor yerine azid ünitelerinin takılma amacı, kopolimerin azid grubu ile PEG-çekirdekde bulunan alkin grubu arasında oluşacak olan CuAAC click reaksiyonunu oluşturabilmektir.

Sonuç polimerinin iskeletini oluşturan ikinci polimer, 2-Bromo-propionik asit 2-(3,5-Dioxo-10-oxa-4-azatrisiklo[5.2.1.02,6]dec-8-en-4-yl) etil ester ile *N*-butil oxanorbornene imid (ONB-butil) monomerleri arasında gerçekleşen ROMP polimerizasyon tekniği ile sentezlenmiş olup, ikinci aşamada sodyum azid eklenerek 24 saat süren bir reaksiyon sonucu azidlenmiş ve Poli(ONB-butil)$_{15}$-*b*-Poli(ONB-Azid)$_5$ sentezlenmiştir. İkinci iskeletimiz olan Poli(ONB-butil)$_{15}$-*b*-Poli(ONB-Azid)$_5$ kopolimerininde de brom üniteleri yerine azid fonksiyonlarını takma amacımız diğer kopolimerle aynıdır.

Sonuç aşamasında, iskelet olarak kullanılacak olan azidli kopolimerler, PCL-TEMPO ve PEG-çekirdek ile one-pot sentezi klik reaksiyonları ile V-şekilli aşı kopolimerleri sentezleri gerçekleşmiştir.

Sonuç polimerlerinin karakterizasyonları başarılı bir şekilde gerçekleştirilmiştir. Kopolimerler literatürdeki prosedürlere uygun bir şekilde başarılı olarak sentezlenmiştir. Sentezlenen V-şekilli iki adet aşı kopolimerlerinin ^{1}HNMR ve GPC analizleri tartışma ve sonuç bölümünde ayrıntılı bir şekilde anlatılacak, her maddenin sentezlenme prosedürü ayrıntı ile verilecek ve hazırlanma aşamaları detaylı olarak anlatılacaktır.

1. INTRODUCTION

Polymer properties are mainly influenced by the chemical composition, functionality, molecular weight and topology of the constituting macromolecules [1]. Therefore, the synthesis of well-defined complex macromolecular structures, such as stars, dendrimers, graft and cyclic polymers, to control the polymer properties is a key field of study in polymer science [1].

Graft copolymers can be obtained with three general methods: (i) grafting-onto, in which side chains are preformed, and then attached to the backbone; (ii) grafting-from, in which the monomer is grafted from the backbone; and (iii) grafting-through, in which the macromonomers are copolymerized [2,3].

The construction of complex macromolecules exhibiting a precise architecture, size, shape, and functionality is a challenging domain with rapidly growing interest [4,5]. Recently, the key points of investigation were centered on the synthesis of graft polymers with complex architectures because of their important roles in understanding the correlation of structure and properties, and exploring new materials [6,7]. In particular, the synthesis of graft polymers with two identical side chains at each graft point, named ‘‘centipede-like’’ graft polymer or ‘‘V-shaped’’ graft polymer, has been reported [6,7].

Xie et al. prepared well-defined centipedelike brush copolymers with amphiphilic PCL and poly(2-(dimethylamino)ethylmethacrylate) as the side chains by combination of ROP, ring-opening metathesis polymerization, and ATRP [8]. However, the studies of such grafted copolymers are still restrained due to the synthetic difficulties. One-pot reaction strategy has been widely applied in the synthesis of different polymer architectures [9-14] which accelerates synthetic procedure and reduces the number of reactions as well as purification steps, therefore leading to more environmentfriendly products. Recently, “click” chemistry has been utilized extensively in polymer and material science to construct various polymer architectures because of its high selectivity, near-perfect reliability, and high yield.

Most importantly, it is exceptionally tolerant toward a wide range of functional groups and reaction conditions [15,16]. Such advantages have been applied for the synthesis of brush copolymers by combination of "click" chemistry with controlled/living polymerization previously.[17,18-22].

In this study, there is a Diels-Alder reaciton between Anthracen-9-ylmetyl-2((2-bromo-2-methylpropanoxy)methyl)2-methyl-3-oxo-3-(prop-2-ynyloxy)-propyl succinate and succinic acid mono-anthracen-9-ylmethyl-ester to synthesize α-alkyne-α-bromide-terminated PEG (PEG-alkyne/Br) which is shown in the figure 1.1. The use of CuAAC and NRC click reactions allowed us to prepare a well-defined V-shaped graft copolymers. The other reactions and their special conditions are explained in other sections.

The synthesis of V-shaped graft copolymers are synthesized via triple click reactions in Figure 1.1.

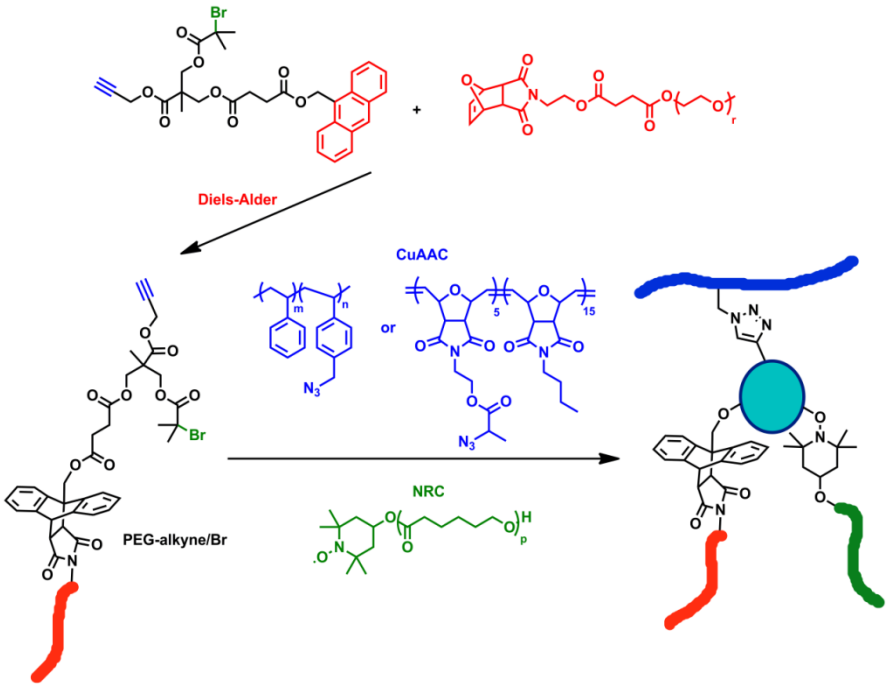


Figure 1.1 : Synthesis of V-shaped graft copolymers via triple click reactions.

2. THEORETICAL PART

2.1 Controlled/Living Polymerization

A living polymerization is defined as a chain polymerization that proceeds in the absence of chain transfer and chain termination as indicated by Szwarc. His pioneering work on the anionic polymerization of St initiated with sodium naphthalenide opened the field of living polymers with controlling the molecular weight and molecular weight distributions as well as the structure of the end-groups. After the discovery of living anionic polymerization, critical research on cationic polymerization was performed in the "living" era**.** An equimolar mixture of HI/I_2 was the first system used for the initiation of such polymerizations of vinyl ethers [23].

Well-defined polymers, can only be synthesized by living ionic polymerizations or controlled/ "living" radical polymerization (C/LRP) methods [24]. Until recently, ionic polymerizations (anionic or cationic) were the only living techniques that efficiently controlled the structure and architecture of vinyl polymers. These polymerization techniques ensure low polydispersity materials, controlled molecular weight and defined chain ends but they are not useful for the polymerization and copolymerization of a wide range of functionalized vinylic monomers [25].

Furthermore, these techniques require stringent reaction conditions and pure reagents. To overcome all these limitations polymer chemists developed new concepts. These new concepts are often called controlled radical polymerization, living radical polymerization, control/"living" radical polymerization [26, 27].

Living polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). To obtain well defined polymers the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [28-30].

Living free radical polymerizations have attained a tremendous following in polymer chemistry. A great deal of effort has been made to develop and understand different living free radical polymerization (C/LRP) methods. Georges and co-workers first introduced true nitroxide mediated polymerization (NMP) in 1993, Matyjaszewski and Sawamoto developed metal catalzed (Cu, Ru) living radical polymerization also called atom transfer radical polymerization (ATRP) in 1995, and Moad, Rizzardo and Thang reported reversible addition-fragmentation chain transfer polymerization (RAFT) in 1998 [31,32,33,34]. various reactivities should be at least as fast as propagation [28-30].

2.1.1 Atom transfer radical polymerization (ATRP)

Metal-catalyzed C/LRP, mediated by Cu, Ru, Ni, and Fe metal complexes, is one of the most efficient methods to produce polymers in the field of C/LRP [35].

Atom transfer radical polymerization (ATRP) is a living radical polymerization process, which is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand. The ATRP system is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand. ATRP, which is the most versatile method of the controlled radical polymerization system, uses a wide variety of monomers, catalysts, solvents, and reaction temperature. ATRP is one of the most convenient methods to synthesize well-defined low molecular weight polymers [36].

A general mechanism for ATRP is shown in Figure 2.1. ATRP is based on the reversible homolytic cleavage of carbon-halogen bond by a redox reaction. Homolytic cleavage of the alkyl (pseudo)halogen bond (RX) by a transition metal complex (activator, M_t^n –Y / ligand, where Y may be another ligand or a counterion) in the lower oxidation state generates an alkyl radical ($R^{\bullet}$) and a transition metal complex (deactivator, $X–M_t^{n+1}$ / ligand) in the higher oxidation state.

The formed radicals can initiate the polymerization by adding across the double bond of a vinyl monomer, propagate, terminate by either coupling or disproportionation, or be reversibly deactivated by the transition metal complex in the higher oxidation state to reform the dormant species and the activator.

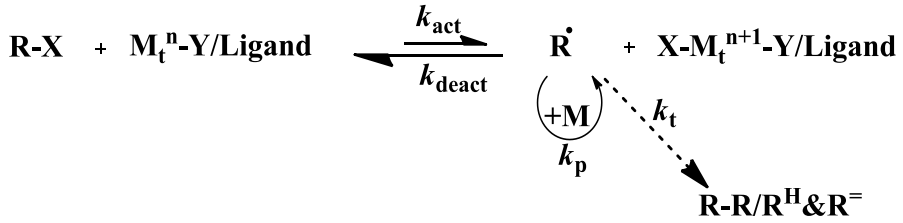


Figure 2.1: General mechanism of atom transfer radical polymerization [37-39].

This process occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}, respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p.

Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination.

Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. Other side reactions may additionally limit the achievable molecular weights.

This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages.

A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation [37-39].

2.1.2 Nitroxide mediated radical polymerization (NMP)

Nitroxide mediated radical polymerization (NMP) is a living polymerization process. It is capable of producing well-defined polymers with narrow molecular weight distribution (MWDs) and predictable molecular weights (MWs).

It is interesting to note a similarity between the iniferter mechanism and the general outline of a successful living free radical mechanism (Figure 2.2).

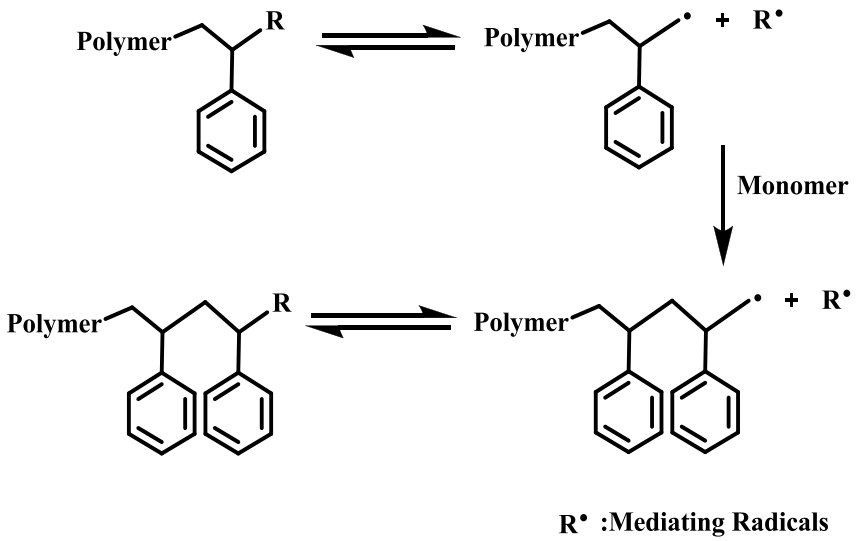


Figure 2.2: General mechanism of nitroxide mediated radical polymerization.

The identity of the mediating radical, R·, is critical to the success of living free radical procedures and a variety of different persistent, or stabilized radicals have been employed. These range from (arylazo)oxy [40], substituted triphenyls,[41] verdazyl [42], triazolinyl [43], nitroxides [44] etc. with the most widely studied and certainly most successful class of compounds being the nitroxides, especially 2,2,6,6-tetramethylpiperidinoxy (TEMPO), and their associated alkylated derivatives, alkoxyamines.

The 2,2',6,6'- tetramethylpiperidine-1-oxyl radical (TEMPO) was used as the nitroxide component in these initial studies. The alkoxyamine is formed in situ during the polymerization process [45]. Although NMP is one of the simplest methods of living free radical polymerization (LFRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry.

The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker et. al. which involves the controlled monoaddition of maleic anhydride or maleimide derivatives to the alkoxyamine chain end. The alkoxyamine can then be easily eliminated and other functional groups can be introduced [46]. to initiator ratio, $[M]_0/[I]_0$ [37, 38, 39].

2.1.3 Reversible addition-fragmentation chain transfer process (RAFT)

Reversible addition-fragmentation chain transfer (RAFT) polymerization is one of the most efficient methods in C/LRP [47, 48].An important advantage of this method over ATRP and NMP is its tolerance to a wide range of functionalities, namely -OH, -COOH, $CONR_2$, NR_2, SO_3Na, etc., in monomer and solvent [48-50].

Reversible addition-fragmentation chain transfer (RAFT) incorporates compounds, usually dithio derivatives, within the living polymerization that react with the propagating center to form a dormant intermediate. The dithio compound can release the alkyl group attached to the opposite sulfur atom which can then propagate with the monomer.

The greatest advantage to RAFT is the incredible range of polymerizable monomers. As long as the monomer can undergo radical polymerization, the process will most likey be compatible with RAFT. However, there are many major drawback that arise when using this process. The dithio end groups left on the polymer give rise to toxicity, color, and odor and their removal or displacement requires radical chemistry. Also, the RAFT agents are expensive and not commercially available. Another drawback is that the process requires an initiator, which can cause undesired end groups and produce too many new chains which can lead to increased termination rates [51].

2.2 Ring Opening Polymerization (ROP)

Aliphatic poly(ester)s receive increasing attention nowadays due to their biodegradable property. Poly(ester)s can be prepared from a wide range of materials with judicious choice of monomer feedstock able to modulate the physio-chemical properties including glass transition temperatures, toughness, stiffness and degradability.

Aliphatic poly(ester)s are prepared through one of two routes: the first is step-growth polycondensation of a hydroxy acid or between a diacid and a diol. The second route is ring-opening polymerization (ROP). It is a unique polymerization process, in which a cyclic monomer is opened to generate a linear polymer, e.g., ROP of ε-caprolactone (CL) (Figure 2.3). ROP is a chain polymerization, comprise of a sequence of initiation, propagation and termination, so different from step

polymerization. Altough ROP like as living polymerization because of increasing molecular weigth linearly with conversion [52], it differs from chain polymerizations due to reaction kinetics. By this methodology the preparation of high molecular weight aliphatic poly(ester)s is possible while maintaining high levels of control over their molecular characteristics under relatively mild conditions.

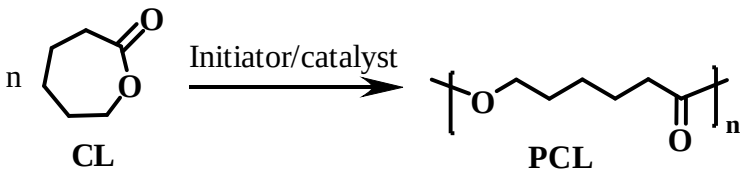


Figure 2.3: ROP of ε-caprolactone (CL) [52].

2.3 The Ring-Opening Metathesis Polymerization (ROMP)

Although relatively new player on the field of polymer chemistry, ring-opening metathesis polymerization (ROMP) has emerged as a powerful and broadly applicable method for synthesizing macromolecular materials.

The origins of ROMP can be traced to the mid-1950s when various metals and reagents were combined to uncover new transformations and reactivities involving olefins.

However, the rapid rise in popularity and utility of this polymerization technique is the result of extensive work on the identification and isolation of key intermediates involved in the general olefin metathesis reaction. This led to the development of well-defined ROMP catalysts and ultimately enabled the synthesis of a wide range of polymers with complex architectures and useful functions [53]

It was only in 1971 that a metal-carbene intermediate was proposed by Y. Chauvin, to explain – satisfactorily for the first time – the mechanism. This extraordinary mechanistic proposal, rationalising Chauvin's astonishing new observations, was immediately embraced by the metathesis community and prompted studies on metal-carbene initiators culminating in the creation of the molybdenum- alkylidene catalysts by R. R. Schrock (Figure 2.4), and the 1st and 2nd generation of ruthenium-alkylidene catalysts, by R. H. Grubbs (Figure 2.5) [54].

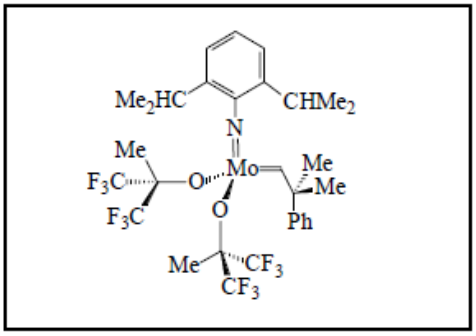


Figure 2.4: Molybdenum- alkylidene catalysts by R. R. Schrock [54].

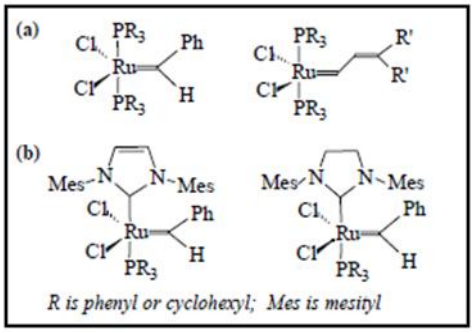


Figure 2.5: The first and second generation of ruthenium-alkylidene catalysts, by R. H. Grubbs [54].

2.4 Click Chemistry

'Click chemistry' is a chemical term introduced by Sharpless in 2001 and describes chemistry tailored to generate substances quickly and reliably by joining small units together [55]. Click chemistry can be summarized only one sentence: Molecules that are easy to make. Sharpless also introduced some criteria in order to fullfill the requirements as reactions that: are modular, wide in scope, high yielding, create only inoffensive by-products, are stereospecific, simple to perform and that require benign or easily removed solvent. Nowadays there are several processes have been identified under this term in order to meet these criterias such as nucleophilic ring opening reactions; non-aldol carbonyl chemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions. Among these selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC) and Diels-Alder (DA) cycloaddition reactions and thiol-ene reactions have gained much interest among the chemists**.**

2.4.1 Diels alder reaction

The Diels-Alder (DA) reaction is a concerted [4π+2π] cycloaddition reaction of a conjugated diene and a dienophile. This reaction is one of the most powerful tools used in the synthesis of important organic molecules. The three double bonds in the two starting materials are converted into two new single bonds and one new double bond to afford cyclohexenes and related compounds (Figure 2.6). This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation [56-58].

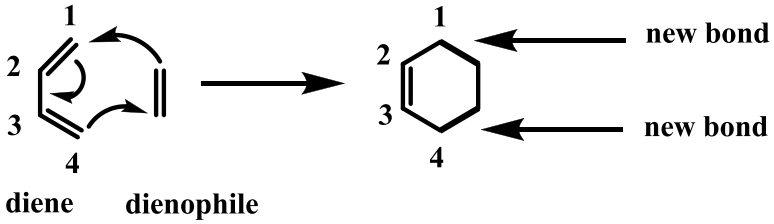


Figure 2.6: General mechanism of diels-alder [56-58].

Typically, the DA reaction works best when either the diene is substituted with electron donating groups (like -OR, -NR2, etc) or when the dienophile is substituted with electron-withdrawing groups (like -NO2, -CN, -COR, etc)[59].

2.4.1.1 Stereochemistry of diels alder reaction

There are stereochemical and electronic requirements for the DA reaction to occur smoothly. First, the diene must be in an s-cis conformation instead of an s-trans conformation to allow maximum overlap of the orbitals participating in the reaction (Figure 2.7)

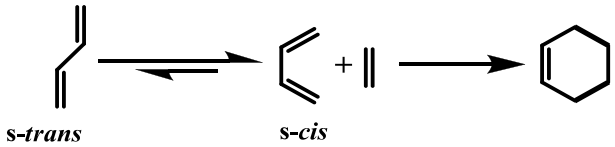


Figure 2.7: Stereochemistry of diels-alder [60,61].

The "s" in s-cis and s-trans refers to "sigma", and these labels describe the arrangement of the double bonds around the central sigma bond of a diene. Dienes often exist primarily in the lower energy s-trans conformation, but the two conformations are in equilibrium with each other. The s-cis conformation is able to react in the DA reaction and the equilibrium position shifts towards the s-cis

conformer to replenish it. Over time, all the s-trans conformer is converted to the s-cis conformer as the reaction proceeds .

A unique type of stereoselectivity is observed in DA reactions when the diene is cyclic. In the reaction of maleic anhydride with cyclopentadiene, for example, the endo isomer is formed (the substituents from the dienophile point to the larger bridge) rather than the exo isomer (the substituents from the dienophile point away from the larger bridge) (Figure 2.8).

The preference for endo–stereochemistry is “observed” in most DA reactions. The fact that the more hindered endo product is formed puzzled scientists until Woodward, Hoffmann, and Fukui used molecular orbital theory to explain that overlap of the p orbitals on the substituents on the dienophile with p orbitals on the diene is favorable, helping to bring the two molecules together [60, 61].

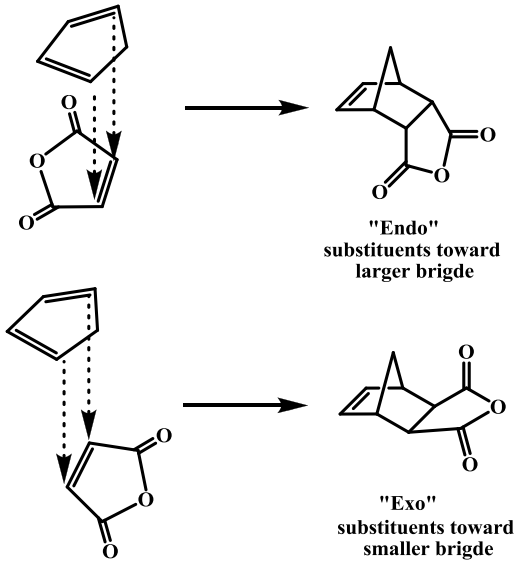


Figure 2.8: Endo and exo izomers [60,61].

Hoffmann and Fukui shared the 1981 Nobel Prize in chemistry for their molecular orbital explanation of this and other organic reactions. In theillustration below, notice the favorable overlap (matching light or dark lobes) of the diene and the substituent on the dienophile in the formation of the endo product (Figure 2.9):

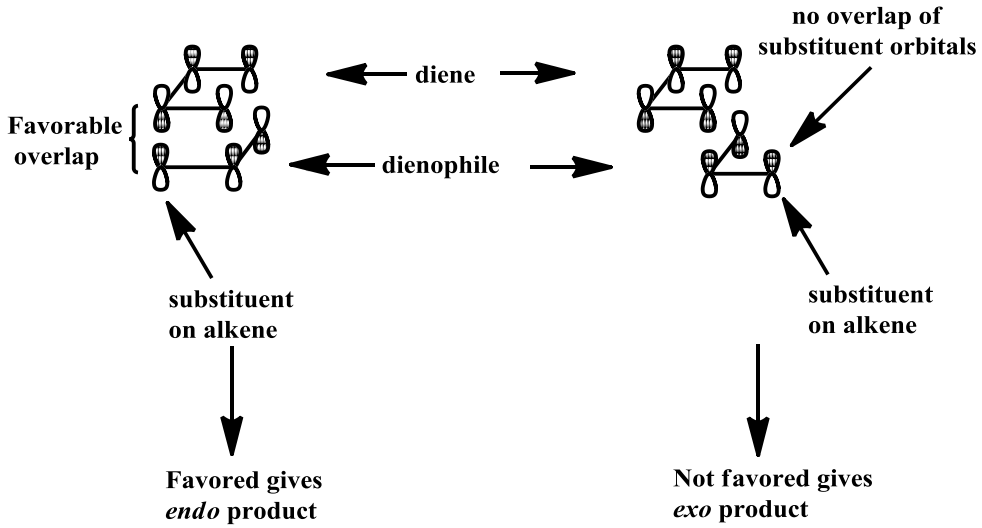


Figure 2.9: Favorable overlap of the diene and the substituent on the dienophile in the formation of the endo product.

Oftentimes, even though the endo product is formed initially, an exo isomer will be isolated from a DA reaction. This occurs because the exo isomer, having less steric strain than the endo, is more stable, and because the DA reaction is often reversible under the reaction conditions. In a reversible reaction, the product is formed, reverts to starting material, and forms again many times before being isolated. The more stable the product, the less likely it will be to revert to the starting material. If the reaction is not reversible under the conditions used, the kinetic product will be isolated. However, if the first formed product is not the most stable product and the reaction is reversible under the conditions used, then the most stable product, called the thermodynamic product, will often be isolated.

2.4.2 Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC)

There is a large class of reactions known as 1,3-dipolar cycloaddition reactions (1,3-DPCA) that are analogous to the Diels-Alder reaction in that they are concerted [4π+2π] cycloadditions [62,63]. 1,3-DPCA reactions can be represented as shown in the following diagram. The entity a-b-c is called the *1,3-dipole* and d-e is the *dipolarophile* (Figure 2.10).

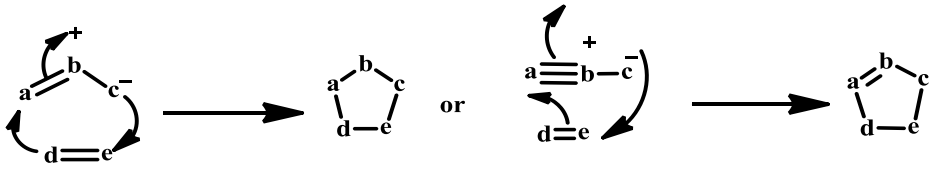


Figure 2.10: General mechanism of CuAAC [64].

The 1,3-dipoles have a π-electron system consisting of two filled and one empty orbital and are analogous with the allyl or propargyl anion. Each 1,3-dipole has at least one charge-separated resonance structure with opposite charges in a 1,3-relationship. It is this structural feature that leads to the name 1,3-dipole for this class of reactants.

The dipolarophiles are typically substituted alkenes or alkynes but all that is essential is a π bond, and other multiply bonded functional groups such as carbonyl, imine, azo, and nitroso can also act as dipolarophiles. The reactivity of dipolarophiles depends both on the substituents present on the π bond and on the nature of the 1,3-dipole involved in the reaction.

Owing to the wide range of structures that can serve either as a 1,3-dipole or as a dipolarophile, the 1,3-DPCA is a very useful reaction for the construction of five-membered heterocyclic rings. At this point, a particular interest must be given to Ralf Huisgen for his pionering works on this field (Huisgen 1,3-DPCA) [64]. In his studies, various five-membered heterocyclic rings such as triazole, triazoline, isoxazole, 4-isoxazoline etc. were described.

The triazole ring, formed via Huisgen 1,3-DPCA reaction between an azide an alkyne have gained much interest due to its chemically inert character e. g. oxidation, reduction and hydrolysis. The reason behind this fact lies in the inert character of the two components (azide and alkyne) to biological and organic conditions. Elevated temperatures and long reaction times are important requirements for the triazole formation as stated by Huisgen. Good regioselectivity in the uncatalyzed Huisgen type cycloaddition is observed for coupling reactions involving highly electron-deficient terminal alkynes, but reactions with other alkynes usually afford mixtures of the 1,4- and 1,5-regioisomers (Figure 2.11) [65].

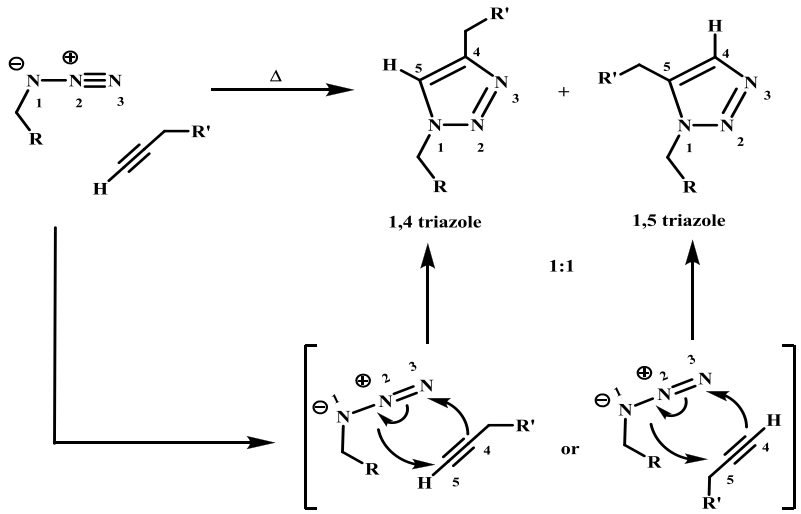


Figure 2.11: Reaction mixtures of the 1,4- and 1,5-regioisomers [65].

Thus, only following the recent discovery of the advantages of Cu(I)-catalyzed alkyne–azide coupling, reported independently by the Sharpless and Meldal groups, did the main benefits of this cycloaddition become clear [66,67]. Cu(I) catalysis dramatically improves regioselectivity to afford the 1,4-regioisomer exclusively (Figure 2.12) and increases the reaction rate up to 10^7 times eliminating the need for elevated temperatures [68]. This excellent reaction tolerates a variety of functional groups and affords the 1,2,3-triazole product with minimal work-up and purification, an ideal click reaction [66,67]. Stepwise cycloaddition catalyzed by a monomeric Cu(I) species lowers the activation barrier relative to the uncatalyzed process by as much as 11 kcal/mol, which is sufficient to explain the incredible rate enhancement observed under Cu(I) catalysis.

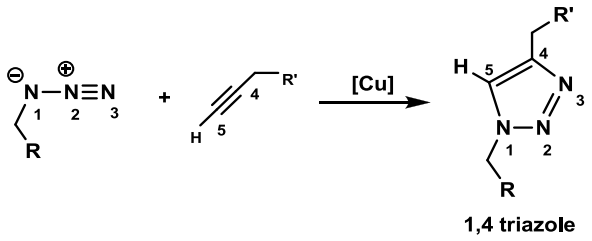


Figure 2.12: Synthesis of 1,4 triazole units [68].

However, if the first formed product is not the most stable product and the reaction is reversible under the conditions used, then the most stable product, called the thermodynamic product, will often be isolated.

2.4.3 Nitroxide radical coupling click (NRC)

A new reversible coupling strategy termed atom transfer nitroxide radical coupling (NRC) [69-76] has the attributes of is a "click" reaction. In which the bromine end-functional group of one polymer served as oxidant is reduced to bromine anion and carbon radical is formed. The Cu^{1+} is oxidized to Cu^{2+} in the presence of CuBr/ ligand. Then polymeric radical is immediately captured by another 2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPO) end-functional polymer, and alkoxyamine is formed between the two polymers [76] (Figure 2.13). In NRC reaction, CuBr participated in the reaction was served as reactant and its action was quite different from the ATRP. If some Cu(0) was added, the Cu(0) would react with the formed Cu^{2+} and the Cu^{+} was regenerated, which promoted the reaction completely. Thus, under the NRC conditions (such as the Cu(0)/CuBr/PMDETA system), the graft, [77] the star-shaped, [78] and the linear copolymer [79] were prepared successfully with high efficiency.

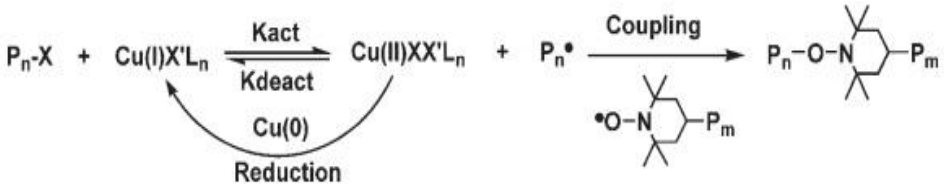


Figure 2.13: General mechanism of nitroxide radical coupling click [76].

This reaction involves formation of a carboncentered radical by an atom transfer reaction with Cu(I)Br and trapping of this radical with a persistent nitroxide radical at close to diffusion-controlled rates. The unique aspect of this reaction is its reversibility, in which the product alkoxyamine can readily be converted to the starting incipient radical and parent nitroxide at elevated temperatures (>100 ^{0}C when TEMPO-type nitroxides are used) [80-82]. This methodology has been used to synthesize degradable and reversibly coupled linear multiblock copolymers, block and graft copolymers in the presence of a 10-fold molar excess of copper species per halide end group [75]. The rate determining step in the coupling reaction is the speed (kact) at which the halide end groups on the polymer chains convert (or are activated) to the carbon-centered radical via atom transfer reactions with Cu(I) species.

2.5 Complex Macromolecular Architecture

'Click chemistry' The improvement of controlled/living polymerization techniques resulted in definitely management many aspects of complex macromolecular architecture in terms of topology, composition and functionality [83-85]. Anionic polymerization is the most precise and powerful methodology [85], but recent progress in C/LRP additionally has opened the possibility of using many unprotected functional monomers [86, 87].

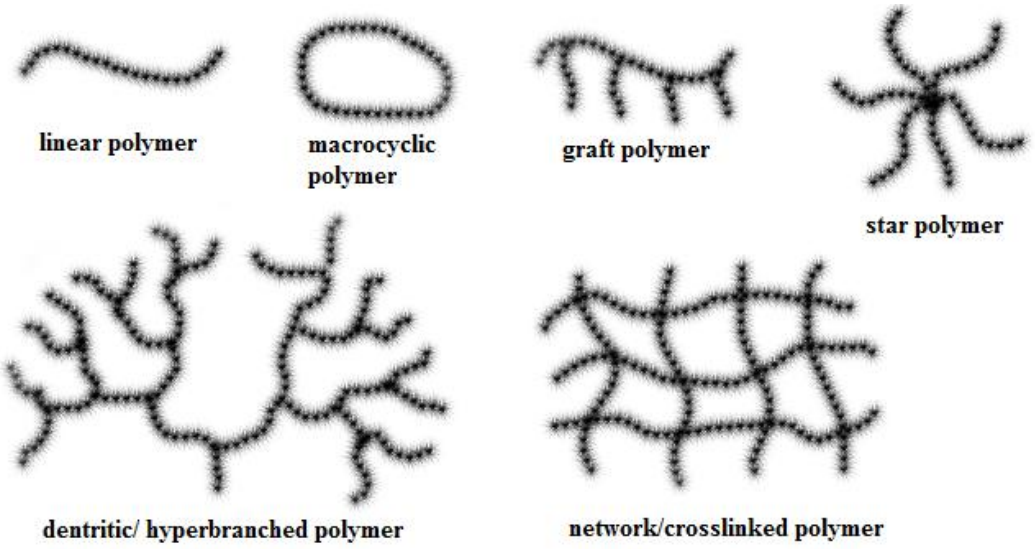


Figure 2.14: Illustration of polymers with various topologies [83-85].

The various C/LRP techniques allow the synthesis of well-defined polymeric materials with different topology, including linear, star, cyclic, brush, branched polymers, and cross-linked networks (gels) (Figure 2.14) cycloaddition reactions and thiol-ene reactions have gained much interest among the chemists**.**

2.5.1 V-Shaped graft copolymers

In this thesis, V-shaped copolymers are synthesized via click chemistry. In the literature, it is mentioned that, a lot of scientists used some tecniques to synthesize V-shaped graft copolymers. These tecniques will shortly summarized by next examples.

In new trend in living polymerization is the synthesis of polymers with nonpolar structures such as graft, arborescent, dendritic and dendrimer-like polymers [88-107].

Qwing to the living nature of anionic polymerization, the structure of subunits in these polymers, such as arms, branches, and grafts, and so forth can be well

controlled in terms of molecular weight and polydispersity. It is also possible to make topological tailoring on the subunits using reactions of anion with some functional compounds. These architectural parameters are very important in the study of structure–property relationship. Specifically, graft (co)polymers with a diversity of architectures such as conventional graft and its block copolymer with linear segments,[108-113] star graft,[113,114] block-graft,[112,115,116] and centipede-type graft [117–123] structures were synthesized by anionic polymerization. These synthetic works employed various methodologies [124].

This kind of copolymers were generally synthesized by ‘‘graft onto’’ method developed by Hadjichristidis [120,121,125 and Hirao [118,123] using chlorosilane or 1,1-diphenylethylene derivatives as coupling agents respectively, but lately Huang et al.[126] obtained the graft copolymers of polyacrylate as backbone and poly (ethylene glycol), polystyrene (PS) as side chains by combination of ‘‘graft through’’ and ‘‘graft from’’ strategies [139]. Hadjichristidis and coworkers developed a chlorosilane coupling technique since a long time, which was then intensively applied in their group to synthesize a variety of polymers with comb-like,[109–111,114,120] starcomb, [113,114,117] comb-on-comb,[114] double combs, [113] ‘‘centipedes,’’ [117,120] block-comb/graft, [115,116] and barbwire- like [120] architectures. These syntheses were fulfilled mostly through a macromonomer strategy[124].

Hirao and coworkers [118,122,123] employed coupling chemistry of polymer anion with benzyl halide to prepare high-density branched polymers carrying two branch chains in each repeating unit (‘‘V-shaped’’ branches) [124].

lnterestingly, Zubarev and coworkers [127–130] synthesized the star-shaped copolymers with the V-shaped poly(butadiene)- poly(ethylene oxide) arms by ‘‘graft onto’’ method and investigated their assemblies. However, for each macromolecule only six arms were coupled onto a small molecule core (Figure 2.15) [124,139].

There are some disadvantages for the preparation of the V-shaped side chains by anionic technology:

1. The linking and purification for each step is a time-consuming process,

2. The efficiency of the linking reaction is unsatisfactory, which is affected by the steric volume of the linking agent and the macromolecular chain,

3. In anionic polymerization for the preparation of the V-shaped side chains, only a limited number of monomers could be used.

Thus, looking for a simple and universal method to prepare the graft copolymers with V-shaped side chains would be interesting for polymer chemists.

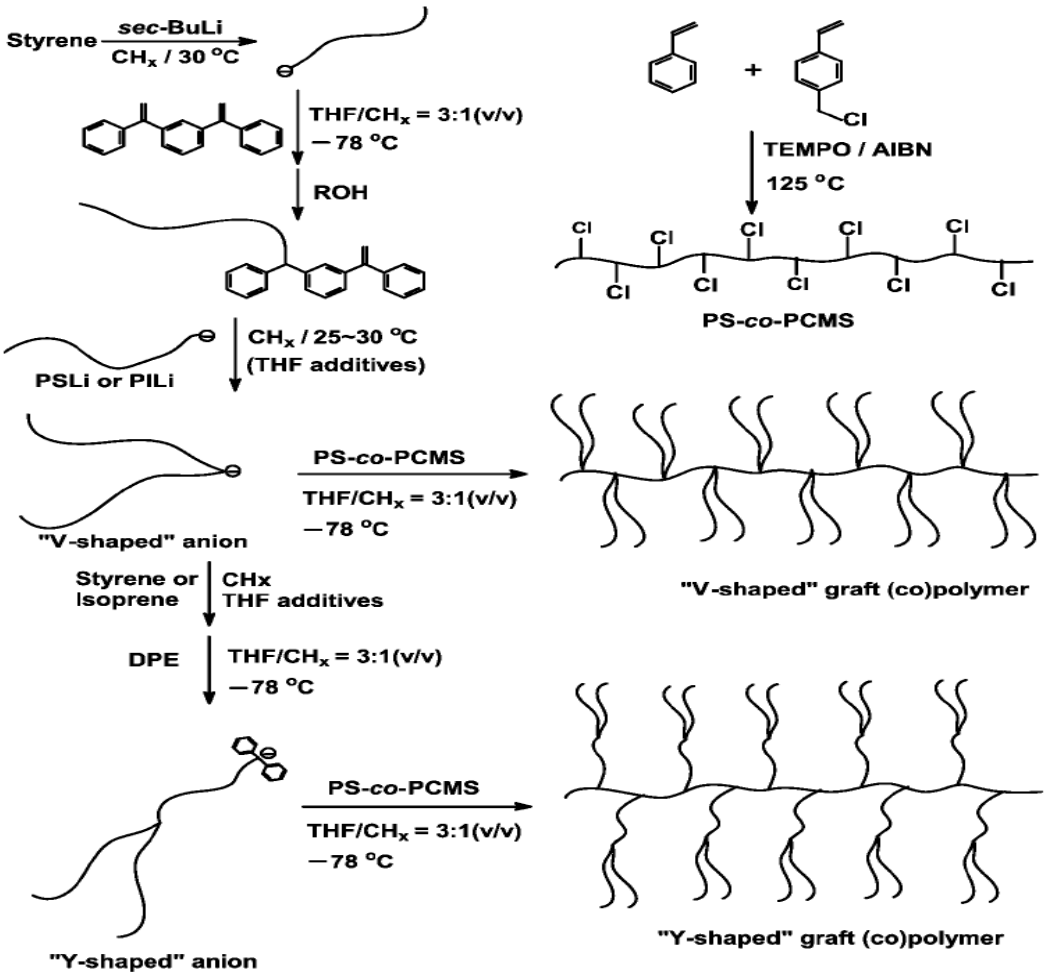


Figure 2.15: Synthetic route of graft copoymers with V-shaped and Y-shaped branches [124].

For example, by using the living/‘‘controlled’’ polymerization techniques as the atom transfer radical polymerization (ATRP), [131] nitroxide-mediated radical polymerization, [132] reversible addition fragmentation transfer polymerization (RAFT), [133] and single electron transfer polymerization, [133-137] as well as the ‘‘click chemistry,’’ [55,138] the graft copolymers with complicated structure could be made [139].

3. EXPERIMENTAL PART

3.1 Materials

Styrene (St, 99 %, Merck) was passed through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuum prior to use. 4-Chloromethylstyrene (CMS; ca. 60/40 meta/paraisomer mixture; 97%; Aldrich) was distilled under reduced pressure. ε-Caprolactone (ε-CL, 99%, Aldrich) was distilled from CaH_2 under vacuum. Poly(ethylene glycol monomethyl ether) (PEG-OH) (M_n = 550 g/mol, Acros) was dried over anhydrous toluene by azeotropic distillation prior to use. *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled over NaOH before use. 4-Hydroxy- tetramethylpiperidine-1-oxyl (TEMPO-OH) (97%, Aldrich), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), propargyl alcohol (99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acros), and CuBr (99.9%, Aldrich) were used as received. CH_2Cl_2 (99.9%, Aldrich) was used after distillation over P_2O_5. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone-metallic sodium. Solvents unless specified here were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received without further purification.

3.2 Instrumentation

The ^1H NMR (500 MHz) spectra were recorded on a Bruker NMR Spectrometer in $CDCl_3$. The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI), and ultraviolet (UV) detectors and four Waters Styragel columns (guard HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles). The effective molecular weight ranges are 2000-4,000,000, 50-100,000, 500-30,000, and 500–20,000, respectively. THF and toluene were used as eluent at a flow rate of 0.3 mL/min at 30 °C and as internal standard, respectively. The apparent molecular weights ($M_{n,GPC}$ and $M_{w,GPC}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear PS standards using PL Caliber

Software from Polymer Laboratories. The second GPC set-up (TD-GPC) with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector including refractive index (RI), dual laser light scattering (DLLS) (λ = 670 nm, 90° and 7°) and a differential pressure viscometer was conducted to measure the absolute molecular weights ($M_{n,TDGPC}$ and $M_{w,TDGPC}$) in THF with a flow rate of 0.5 mL/min at 35 °C. Three detectors were calibrated with a PS standard with narrow molecular weight distribution (M_n = 115,000 g/mol, M_w/M_n = 1.02, [η] = 0.519 dL/g at 35°C in THF, dn/dc = 0.185 mL/g) provided by Viscotek company. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2. dc = 0.185 mL/g) provided by Viscotek company. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2.

3.3 Synthesis Methods

4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione, 1 **[**140], 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione, **2** **[**140], 4-(2-{[(3-acetyl-7-oxabicyclo [2.2.1]hept-yl)carbonyl]amino} ethoxy)-4-oxobutanoic acid, **3** **[**140], furan-protected maleimide-terminated poly(ethylene glycol) (PEG-MI), **4** **[**141], succinic acid mono-anthracen-9-ylmethyl-ester, **5** **[**142], Propargyl-2,2,5-trimethyl-1,3-dioxane-5-carboxylate, **7** [143], Propargyl-3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate, **8** [143], Propargyl-3-[(2-bromo-2-methylpropanoyl)oxy-2-(hyroxymethyl)-2-methyl propanoate, **9** [143], Anthracen-9-ylmetyl-2((2-bromo-2-methylpropanoxy) methyl)2-methyl-3-oxo-3-(prop-2-ynyloxy)-propyl Succinate (CORE), **10** [144], tetramethylpiperidine-1-oxyl-terminated poly(ε-caprolactone) (TEMPO-PCL), **12** [145], 2-Bromo-Propionic Acid 2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl) Ethyl Ester, **13** [146], and *N*-butyl oxanorbornene imide (ONB-butyl), **14** [147] were synthesized according to literature procedures**.**

3.3.1 4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (1)

Maleic anhydride (60.0 g, 0.6 mol) was suspended in 150 mL of toluene and the mixture warmed to 80 °C. Furan (66.8 mL, 0.9 mol) was added via syringe and the turbid solution was stirred for 6 h. The mixture was then cooled to ambient

temperature white solids formed during standing were collected by filtration and washed with 2 × 30 mL of petroleum ether and once with diethyl ether (50 mL) afforded 1 as white needless. Yield: 80.2 g (80%). Mp: 114-115 ^{o}C (DSC). ^{1}H NMR ($CDCl_3$, δ) 6.57 (s, 2H, C*H*=C*H*, bridge protons), 5.45 (s, 2H, -C*H*O, bridge-head protons), 3.17 (s, 2H, C*H*-C*H*, bridge protons). ^{13}C NMR ($CDCl_3$, δ) 170.18, 137.29, 82.46, 48.88. Mass spectrometry (+EI) *m*/*z* (%): 167 [MH+] (50), 144 (35), 130 (20).

3.3.2 4 -(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (2)

The adduct 1 (10.0 g, 60.0 mmol) was suspended in methanol (150 mL) and the mixture cooled to 0 °C. A solution of ethanolamine (3.6 mL, 60 mmol) in 30 mL of methanol was added dropwise (10 min) to the reaction mixture, and the resulting solution was stirred for 5 min at 0 °C, then 30 min at ambient temperature, and finally refluxed for 6 h. After cooling the mixture to ambient temperature, solvent was removed under reduced pressure, and residue was dissolved in 150 mL of CH_2Cl_2 and washed with 3 × 100 mL of water. The organic layer was separated, dried over Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave white-off solid which was further purified by flash chromatography eluting with ethylacetate (EtOAc) to give the product as a white solid. Yield: 4.9 g (40%). Mp = 138-139 °C (DSC). ^{1}H NMR ($CDCl_3$, δ) 6.51 (s, 2H, C*H*=C*H*, bridge protons), 5.26 (s, 2H, -C*H*O, bridge-head protons), 3.74-3.68 (m, 4H, NC*H*$_2$C*H*$_2$OH), 2.88 (s, 2H, C*H*-C*H*, bridge protons). ^{13}C NMR ($CDCl_3$, δ) 177.03, 136.60, 81.09, 60.53, 47.74, 42.03. Mass spectrometry (+EI) *m*/*z* (%): 210 [MH+] (50), 145 (22), 142 (100), 124 (17).

3.3.3 Synthesis of 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl)carbonyl]amino} ethoxy)-4-oxobutanoic acid (3)

2 (5 g, 23.9 mmol) was dissolved in 150 mL of 1,4-dioxane. To the reaction mixture were added Et_3N (16.58 mL, 119.6 mmol), DMAP (4.38 g, 35.8 mmol), and succinic anhydride (9.56 g, 95.6 mmol) in that order. The reaction mixture was stirred for overnight at 50 ^{o}C, then poured into ice-cold water and extracted with CH_2Cl_2. The organic phase was washed with 1 M HCl, dried over Na_2SO_4 and concentrated. The crude product was crystallized from ethanol to give **3** as white crystal. Yield: 5.9 g (80%). M.p. = 122-123 ^{o}C (DSC). ^{1}H NMR ($CDCl_3$, δ) 6.50 (s, 2H, C*H*=C*H*, bridge protons), 5.25 (s, 2H, -C*H*O, bridge-head protons), 4.25 (t, *J* = 5.2 Hz, 2H,

$NCH_2CH_2OC=O$), 3.74 (t, *J* =5.2 Hz, 2H, $NCH_2CH_2OC=O$), 2.87 (s, 2H, C*H*-C*H*, bridge protons), 2.66-2.53 (m, 4H, $C=OCH_2CH_2C=OOH$). ^{13}C NMR ($CDCl_3$, δ) 177.26, 176.35, 172.01, 136.83, 81.09, 61.22, 47.74, 37.92, 29.24. Mass spectrometry (+EI) *m*/*z* (%): 310 [MH+] (100), 242 (100), 142 (18), 124 (13).

Ref aynı. 42.03. Mass spectrometry (+EI) *m*/*z* (%): 210 [MH+] (50), 145 (22), 142 (100), 124 (17).

3.3.4 Prepatation of furan-protected maleimide-terminated poly(ethylene glycol) (PEG-MI) (4)

Poly(ethylene glycol)methyl ether (Me-PEG) (M_n = 550) (2.67 g, 4.85 mmol) was dissolved in 50 mL of CH_2Cl_2. To the reaction mixture were added DMAP (0.59 g, 4.83 mmol) and **3** (3 g, 9.71 mmol) in that order. After stirring 5 min at room temperature, a solution of DCC (2 g, 9.69 mmol) in 10 mL of CH_2Cl_2 was added. Reaction mixture was stirred for overnight at room temperature. After filtration off the salt, the solution was concentrated and the viscous brown color product was purified by column chromatography over silica gel eluting with CH_2Cl_2/EtOAc mixture (1:1, v/v) and then with CH_2Cl_2/methanol (90:10, v/v) to obtain MI-PEG as viscous brown oil. Yield: 2.7 g (88%). $M_{n,theo}$ = 840, $M_{n,NMR}$ = 850, $M_{n,GPC}$ = 1300, M_w/M_n = 1.01, relative to PS standards). ^1H NMR (500 MHz, $CDCl_3$, δ) 6.50 (s, 2H, C*H*=C*H* as bridge protons), 5.25 (s, 2H, -C*H*O, bridge-head protons), 4.23 (m, 4H, $CH_2OC=O$), 3.75-3.51 (m, OCH_2CH_2 repeating unit of PEG, $C=ONCH_2$, and CH_2-PEG repeating unit), 3.36 (s, 3H, PEG-OCH_3), 2.87 (s, 2H, C*H*-C*H*, bridge protons) 2.61-2.56 (m, 4H, $C=OCH_2CH_2C=O$).

3.3.5 Synthesis of succinic acid mono-anthracen-9-ylmethyl-ester (5)

9-Anthracene methanol (4.16 g, 20 mmol) was dissolved in 150 mL of CH_2Cl_2. To the reaction mixture were added Et_3N (14 ml, 100 mmol), DMAP (2.44 g, 20 mmol) and succinic anhydride (8 g, 80 mmol) in that order. The mixture was stirred for overnight at room temperature. After that time, the reaction solution was poured into ice-cold water (150 mL), stirred for 30 min. at room temperature before taking into seperating funnel. The organic phase was extracted with 1M HCl (150 mL). The aqueous phase extracted with CH_2Cl_2 and combined organic phases dried over Na_2SO_4 and concentrated to give **5** as a green solid. Yield: 5.85 g (95%). M.p. = 130-131 ^oC (DSC). ^1H NMR ($CDCl_3$, δ) 8.50 (s, 1H, Ar*H* of anthracene), 8.32 (d, *J* = 8.8

Hz, 2H, Ar*H* of anthracene), 8.02 (d, *J* = 8.2 Hz, 2H, Ar*H* of anthracene), 7.60-7.45 (m, 4H, Ar*H* of anthracene), 6.18 (s, 2H, CH_2-anthracene), 2.69-2.62 (m, 4H, C=OCH_2CH_2C=OOH).^{13}C NMR ($CDCl_3$, δ) 177.72, 172.46, 131.57, 131.35, 129.29, 129.07, 127.01, 126.05, 125.41, 124.04, 59.39, 29.01. Mass spectrometry (+EI) *m*/*z* (%): 308 [MH+] (65), 307 (92), 290 (30), 277 (47), 207 (58), 191 (100), 179 (25).

3.3.6 Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid (6)

The 2,2-bis(hydroxymethyl)propanoic acid (8 g, 59.6 mmol) along with *p*-TSA (0.45 g, 2.32 mmol), and 2,2-dimethoxypropane (11.2 mL, 89.4 mmol) dissolved in 40 mL of dry acetone, and stirred 2h at room temperature. In the vicinity of 2h, while stirring continued the reaction mixture was neutralized with 6 mL of totally NH_4OH (25%), and absolute ethanol (1:5), filtered off by-products and subsequent dilution with dichloromethane (100 mL), and once extracted with distilled water (40 mL). The organic phase dried with Na_2SO_4, concantrated to yield 7.4 g (71%) as white solid after evaporation of the solvent. ^{1}H NMR ($CDCl_3$, δ) 4.18 (d, 2H, CCH_2O), 3.63 (d, 2H, CCH_2O), 1.38 (s, 3H, CCH_3) 1.36 (s, 3H, CCH_3), 1.18 (s, 3H, C=OC$(CH_2O)_2CH_3$).

3.3.7 Synthesis of propargyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (7)

Propargyl alcohol (4.9 mL, 85 mmol) was dissolved in 70 mL of CH_2Cl_2 and 2,2,5-trimethyl- [1,3]dioxane-5-carboxylic acid (9.9 g, 57 mmol), and DMAP (3.4 g, 28 mmol) was added to the reaction mixture in that order. After stirring 5 min at room temperature, DCC (14 g, 68 mmol) dissolved in 30 mL of CH_2Cl_2 was added. Reaction mixture was stirred overnight at room temperature and urea byproduct was filtered. Then, reaction mixture was extracted with water/ CH_2Cl_2 (1:4) two times, and combined organic phase was dried with Na_2SO_4. Solvent was evaporated and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (9:1) to give pale yellow oil (yield = 8.1 g; 67%). ^{1}H NMR ($CDCl_3$, δ) 4.72 (d, *J* = 2.4 Hz, 2H, CH≡CCH_2O), 4.18 (d, *J* = 11.6 Hz, 2H, CCH_2O), 3.63 (d, *J* = 11.6 Hz, 2H, CCH_2O), 2.45 (t, *J* = 2.4 Hz, 1H, CH≡CCH_2O), 1.40 (s, 3H, CCH_3) 1.36 (s, 3H, CCH_3), 1.18 (s, 3H, C=OC$(CH_2O)_2CH_3$). ^{13}C NMR ($CDCl_3$, δ) 173.47 (C=O), 98.11 ($CCH_3)_2$, 76.58 (CH≡CCH_2O), 73.03 (CH≡CCH_2O), 65.84 (CH_2O), 52.35 (CH≡CCH_2O), 49.96 (CCH_3), 25.68 (CCH_3), 23.66 (CCH_3), 17.37 (C=OC$(CH_2O)_2CH_3$).

3.3.8 Synthesis of propargyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoat (8)

7, (4.0 g, 19 mmol) was dissolved in a mixture of 10 mL of THF and 10 mL of 1 M HCl. The reaction mixture was stirred for 2 h at room temperature. The precipitated product was filtered off, and reaction mixture was concentrated and extracted with 160 mL of CH_2Cl_2 and 40 mL of water. The combined organic phase was dried with Na_2SO_4 and conc. Hexane was added to the reaction mixture, and it was kept in deep freeze overnight to give white solid, *M*p = 50 °C (yield = 3.1 g, 95%). ^{1}H NMR ($CDCl_3$, δ) 4.72 (d, *J* = 2.4 Hz, 2H, CH≡CC*H*$_2$O), 3.88 (d, *J* = 11.3 Hz, 2H, C*H*$_2$OH), 3.69 (d, *J* = 11.3 Hz, 2H, C*H*$_2$OH), 2.93 (br, 2H, OH), 2.48 (s, 1H, C*H*≡CCH$_2$O), 1.07 (s, 3H, C*C*H$_3$). ^{13}C NMR ($CDCl_3$, δ) 175.08 (C=O), 76.56 (CH≡*C*CH$_2$O), 73.28 (*C*H≡CCH$_2$O), 67.70 (*C*H$_2$OH), 52.52 (*C*CH$_3$), 50.04 (CH≡C*C*H$_2$O), 18.05 (C*C*H$_3$).

3.3.9 Synthesis of propargyl-3-[(2-bromo-2-methylpropanoyl)oxy-2-(hyroxymethyl)-2-methylpropanoate (9)

8, (0.90 g, 5.2 mmol) was dissolved in 15 mL of CH_2Cl_2, and triethyl amine (1.60 mL, 11.5 mmol) was added to the mixture and cooled to 0 °C. 2-Bromo isobutrylbromide (0.65 mL, 5.2 mmol) in 5 mL of CH_2Cl_2 was added dropwise within 30 min. The reaction mixture was stirred 4 h at room temperature. After filtration, the mixture was extracted with CH_2Cl_2 and saturated aq. $NaHCO_3$. The aqueous phase was again extracted with CH_2Cl_2, and combined organic phase was dried with Na_2SO_4. The solution was concentrated, and the crude product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (4:1) to give pale yellow oil (yield = 1.25 g, 75%). ^{1}H NMR ($CDCl_3$, δ) 4.72 (d, *J* = 2.4 Hz, 2H, CH≡C*C*H$_2$O), 4.43 and 4.30 (dd, *J* = 11.2 Hz, 2H, C*H*$_2$OC=O), 3.75 (d, *J* = 6.3 Hz, 2H, C*H*$_2$OH), 2.47 (t, *J* = 2.4 Hz, 1H, C*H*≡CCH$_2$O), 2.33 (br, 1H, OH), 1.91 (6H, CBr(C*H*$_3$)$_2$), 1.27 (s, 3H, (s, 3H, C*C*H$_3$). ^{13}C NMR (CDCl3,δ) 173.28 (C=O), 171.50 (C=O), 76.53 (CH≡*C*CH$_2$O), 75.29 (*C*H≡CCH$_2$O), 66.93 (*C*H$_2$OC=O), 64.93 (*C*H$_2$OH), 55.42 (*C*Br(CH$_3$)$_2$), 52.54 (*C*CH$_3$), 48.54 (CH≡C*C*H$_2$O), 30.66 (CBr(*C*H$_3$)$_2$), 17.26 (C*C*H$_3$).

3.3.10 Synthesis of anthracen-9-ylmetyl-2((2-bromo-2-methylpropanoxy)methyl)2-methyl-3-oxo-3-(prop-2-ynyloxy)-propyl succinate (core) (10)

Compounds **5** (1.72 g, 5.60 mmol) and **9** (1.50 g, 4.67 mmol) were dissolved in 30 mL of CH_2Cl_2 in a flask. DMAP (0.57 g, 4.67 mmol) was then added to the reaction mixture. After stirring for 5 min, DCC (1.15 g, 5.60 mmol) dissolved in 10 mL of CH_2Cl_2 was added to the reaction medium and the mixture was stirred overnight at room temperature. After filtration the solvent was removed and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (4:1) gradually increased to 2:1 to give **10** as a yellow viscous oil (Yield = 2.5 g, 88%). ^{1}H NMR (250 MHz, $CDCl_3$, δ) 8.5 (s, 1H, Ar*H* of anthracene), 8.3 (d, 2H, Ar*H* of anthracene), 8.0 (d, 2H, Ar*H* of anthracene), 7.6–7.3 (m, 4H, Ar*H* of anthracene), 6.1 (s, 2H, C*H*$_2$-anthracene), 4.7 (s, 2H, HC≡CC*H*$_2$O), 4.2 (m, 4H, C*H*$_2$OC=O), 2.6 (s, 4H, C=OC*H*$_2$C*H*$_2$C=O), 2.4 (s, 1H, *H*C≡CCH$_2$O), 1.9 (6H, CBr(C*H*$_3$)$_2$), 1.2 (s, 3H, C*C*H$_3$).

3.3.11 Synthesis of α-alkyne-α-bromide-terminated PEG (PEG-alkyne/Br) via diels-alder click reaction of PEG-MI with 6 (11)

Compound **10** (0.72 g, 1.178 mmol) was dissolved in 10 mL of toluene and PEG-MI (0.5 g, 0.588 mmol, $M_{n,NMR}$ = 850 g/mol) in 10 mL of toluene was added to this solution. The mixture was bubbled with nitrogen for 60 min and refluxed for 24 h at 110 ^{o}C in the dark. After this time, the solution was evaporated to dryness and the viscous dark brown color product was purified by column chromatography over silica gel eluting with a CH_2Cl_2/ethyl acetate mixture (1:1, vol/vol) and then with CH_2Cl_2/MeOH (0.9:0.1) to obtain a dark pink product. The obtained product was dried in a vacuum oven at 40 ^{o}C for 24 h ($M_{n,theo}$ = 775 g/mol ($M_{n,theo}$ of furan-deprotected PEG-MI) + 611 g/mol (MW of **10**) = 1385 g/mol, $M_{n,GPC}$ = 1100 g/mol, M_w/M_n = 1.06, relative to PS standards).

^{1}NMR (500 MHz, $CDCl_3$, δ), 7.4-7.1 (m, 8H Ar*H*), 5.5 (bs, 2H, C*H*$_2$-Diels-Alder adduct), 4.7 (m, 3H, C*H*, bridge head proton and CH≡CC*H*$_2$O), 4.3-4.2 (m, 6H, C*H*$_2$OC=O and C=OOC*H*$_2$), 3.8–3.0 (m, OC*H*$_2$C*H*$_2$, PEG repeating unit, C=OOC*H*$_2$CH$_2$N, C=OOCH$_2$C*H*$_2$N, OC*H*$_3$ end-group of PEG and C*H*-C*H* bridge

protons), 2.7-2.5 (m, 9H, C=OCH_2CH_2C=O, C=OCH_2CH_2C=O and HC≡CCH_2O), 1.9 (6H, CBr(CH_3)$_2$), 1.3 (s, 3H, CCH_3). 1.2 (s, 3H, CCH$_3$).

3.3.12 Synthesis of tetramethylpiperidine-1-oxyl-terminated poly(ε-caprolactone) (TEMPO-PCL) (12)

PCL TEMPO was prepared by ROP of ε-CL (5.0 mL, 0.047 mol) in bulk using tin(II)-2-ethylhexanoate as a catalyst and 4-hyroxy-TEMPO (0.27 g, 1.6 mmol) as an initiator at 110 °C for 3 h, The degassed monomer, catalyst, and initiator were added to a previously flamed Schlenk tube equipped with a magnetic stirring bar in the order mentioned. The tube was degassed with three FPT cycles, left in argon, and placed in a thermostated oil bath. After the specified time, the mixture was diluted with THF, and precipitated into an excess amount of cold methanol. The polymer was isolated by filtration and finally dried at 40 °C in a vacuum oven for 24 h ($[M]_0/[I]_0$ = 30; conv. % = 70; $M_{n,theo}$ = 1790 ; $M_{n,GPC}$ = 3780 ; M_w/M_n = 1.14, relative to PS standards) $M_{n,PCL} = 0.259 \times M_{n,GPC}^{1.073}$ = 1790).

3.3.13 Synthesis of 2-Bromo-Propionic Acid 2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl) ethyl ester(13)

It is sytthesized according to the published procedure.

3.3.14 Synthesis of *N*-butyl oxanorbornene imide (ONB-butyl) (14)

A mixture of 1-bromobutane (1.36 g, 9.925 mmol), potassium carbonate (1.37 g, 9.925 mmol), and compound **1** (1.103 g, 6.625 mmol) was stirred in anhydrous DMF (100 mL) at 50 °C for 4 h. The reaction mixture was evaporated to dryness, and the crude product was purified by chromatography (SiO_2, hexane/ethyl acetate) 1/1). Pure **14** was obtained as a white solid. Yield: 4.99 g (1.25 mmol, 80%). ^{1}H NMR ($CDCl_3$): δ 6.45 (s, 2H), 5.19 (s, 2H), 3.38 (t, 2H), 2.77 (s,2H), 1.53-1.38 (m, 2H), 1.28-1.10 (m, 4H), 0.80 (t, 3H). 13C NMR ($CDCl_3$): δ 176.1, 136.4, 80.7, 47.2, 38.8, 31.1, 27.4, 26.1, 22.3, 13.8.

3.3.15 Synthesis of poly(ONB-butyl)$_{15}$-*b*-poly(ONB-Azide)$_5$ copolymer via ROMP of monomers 2 and 3 (15)

The first generation Grubbs' catalyst (PCy$_3$)$_2$(Cl)$_2$-RuCHPh (0.124 g, 0.15 mmol) was placed in a Schlenk tube and dissolved in 2 mL of anhydrous $CHCl_3$ in a glove

box. The first ROMP monomer **(13)** (0.26 g, 0.755 mmol) and the second ROMP monomer **(14)** (0.5 g, 2.26 mmol) were dissolved in 6 mL of anhydrous $CHCl_3$ in another Schlenk tube and added to the catalyst solution via syringe. The flask was capped with a septum and removed from glove box. The polymerization was allowed to stir at room temperature for 2 hours. The polymerization was then terminated by the addition of butyl vinyl ether, and stirred for additional 1 h at room temperature. Finally, the polymer solution was precipitated in methanol and the obtained polymer was dried for 24 h in a vacuum oven at 40 ^{o}C (2/3/catalyst=15/5/1; conv. (%)=100%; Mn,theo = 5000; Mn,GPC = 6645; Mw/Mn = 1.18, RI detector, relative to PS standards).

^{1}H NMR (500 MHz, $CDCl_3$, δ) 6.1 (bs, C=C*H*, trans), 5.8 (bs, C=C*H*, cis), 5.0 (bs, C*H*O, cis), 4.5-4.3 (bs, C*H*O, trans, OCH_2CH_2N and C*H*Br), 3.8 (bs, OCH_2CH_2N) 3.5-3.3 (bs, N-CH_2, C*H*-C*H* bridge-protons), 2.0-0.5 (m, aliphatic protons).

The previously obtained polymer (0.76 g, 0,15 mmol, Mn,theo=5000) was dissolved in DMF (10 mL) and NaN_3 (0,2 g, 3 mmol) was added to the reaction mixture. After stirring the reaction mixture overnight at room temperature, the product was precipitated in an excess amount of methanol. The crude product was dissolved in THF and reprecipitated in methanol. The dissolution-precipitation was repeated two times. The obtained polymer was dried for 24 h in a vacuum oven at 40 ^{o}C (Mn,GPC =6050; Mw/Mn =1.17, RI detector, relative to PS standards). FTIR (cm_1): 2113 (s) (azide stretching).

^{1}NMR (500 MHz, $CDCl_3$, δ) 6.1 (bs, C=C*H*, trans), 5.8 (bs, C=C*H*, cis), 5.0 (bs, C*H*O, cis), 4.5-4.3 (bs, C*H*O, trans, OCH_2CH_2N), 3.8 (m, OCH_2CH_2N and C*H*N_3) 3.5-3.3 (bs, N-CH_2, C*H*-C*H* bridge-protons), 2.0-0.5 (m, aliphatic protons).

3.3.16 Preparation of copolymers of St and 4-chloromethylstyrene P(S-*co*-CMS) (16)

P(S-*co*-CMS) copolymer was prepared via NMP of St and CMS at 125 ^{o}C with a feed ratio of 10 mol % CMS. In a 25 mL of Schlenk tube, St (3 mL, 26 mmol), CMS (0.409 mL, 2.9 mmol), TEMPO (0.0909 g, 0.581 mmol) and AIBN (0.047 g, 0.290 mmol) were added, the reaction mixture was degassed by three FPT cycles. The tube was then placed in a thermostated oil bath at 125 ºC for 12 h. The polymerization mixture was precipitated in methanol and dried for 24 h in a vacuum oven at 40 ºC.

(Yield: 1.8 g). ^{1}H NMR ($CDCl_3$, δ) 7.5-6.5 (ArH of PS), 4.5 (Ph-CH_2Cl), 2.2-0.6 (aliphatic protons. ($M_{n,theo}$ = 5600; $M_{n,NMR}$ = 5600; $M_{n,GPC}$ = 6050; M_w/M_n = 1.1, relative to PS standards).

Next, the result copolymer (1.8 g, $M_{n,theo}$ = 5600; $M_{n,NMR}$ = 5600; $M_{n,GPC}$ = 6050) dissolved in DMF (15 mL) and NaN_3 (2.92 g, 45 mmol) was added to 50 mL the flask. After stirring overnight at room temperature, the mixture was precipitated into an excess amount of methanol. The recovered polymer P(St_{48}-$Azide_5$) was dried in a vacuum oven at 40 °C for 24 h (Yield = 1,6 g, Mn,GPC = 5600 g/mol; Mw/Mn = 1.19 , relative to PS standards). 1H NMR (CDCl3, δ), 3.9 (br, 2H, CH(Ph)-N3 end group of PS), 3.4 (br, 4H, OCH2CH2O), 2.2-0.8 (m, aliphatic protons of PS).

3.3.17 One-pot synthesis of V-shaped P(St_{48}-$Azide_5$)-*g*-(PEG-PCL) through NRC and CuAAC click reactions of P(St_{48}-$Azide_5$) and PCL-TEMPO with PEG-alkyne/Br

PEG-alkyne/Br (0.185 g, 0.134 mmol, $M_{n,theo}$ = 1385 g/mol, 7.5 equiv), P(S_{48}-$Azide_5$) (0.1 g, 0.0179 mmol, $M_{n,GPC}$ = 5600 g/mol, 1 equiv) and PCL-TEMPO (0.24 g, 0.134 mmol, $M_{n,PCL}$ = 1790 g/mol, 7.5 equiv) were dissolved in a 8 mL of nitrogen-purged DMF in a Schlenk tube. CuBr (0.0128 g, 0.089 mmol), Cu(0) (0.0284 g, 0.446 mmol), and PMDETA (0.0186 mL, 0.089 mmol) were added to the solution, and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles, left in argon and stirred at room temperature for 12 h. After this specified time, the polymer solution was passed through alumina column to remove copper salt and precipitated in methanol (0.19 g). Next, the crude product was dissolved in THF and precipitated in methanol (0.17 g). The dissolution-precipitation was repeated two times. Finally, the polymer was dried in a vacuum oven at 40 ^{o}C ($M_{n,theo}$ = 21480 g/mol (a sum of theoretical MWs of individual arms), $M_{n,NMR}$= 18135 g/mol, $M_{n,GPC}$ = 14800 g/mol, M_w/M_n = 1.18, relative to PS standards).

^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.4 (s, 1H, C*H* of triazole), 7.3-6.2 (Ar*H* of PS), 5.5 (br, 2H, CH_2-Diels-Alder adduct), 5.0 (br, 3H, triazole- CH_2OC=O and C*H* of TEMPO), 4.7 (s, 1H, C*H*, bridge head proton), 4.3-4.2 (m, 6H, CH_2OC=O and C=OOCH_2), 4.0 (bs, CH_2O of PCL), 3.6-3.4 (bs, OCH_2CH_2 of PEG C=OOC$H_2$$CH_2$N and C=O$OCH_2CH_2$N), 3.4–3.1 (m, 5H, OC$H_3$ end group of PEG and C*H*-C*H* bridge

protons), 2.6-2.2 (br, 8H, OC=OCH_2CH_2C=OO), 2.2 (bs, C=OCH_2 of PCL), 2.0–0.5 (m, aliphatic protons of PS and PCL).

3.3.18 One-pot synthesis of V-shaped P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$)-*g*-(PEG-PCL) through CuAAC and NRC click reactions of poly(ONB-butyl)$_{15}$-poly(ONB-Azide)$_5$ and PCL-TEMPO with PEG-alkyne/Br

PEG-alkyne/Br 0.311 g, 0.225 mmol, $M_{n,theo}$ = 1385 g/mol, 7.5 equiv), PONB-N_3 (0.15 g, 0.03 mmol, $M_{n,theo}$ = 5000 g/mol, 1.0 equiv) and PCL-TEMPO (0.403 g, 0.225 mmol, $M_{n,PCL}$ = 1790 g/mol, 7.5 equiv) were dissolved in a 8 mL of nitrogen-purged DMF in a Schlenk tube. CuBr (0.021 g, 0.15 mmol), Cu(0) (0.048 g, 0.75 mmol), and PMDETA (0.0313 mL, 0.15 mmol) were added, and the reaction mixture was degassed by three FPT cycles, left in argon and stirred at room temperature for 12 h. After this specified time, the polymer solution was passed through alumina column to remove copper salt and precipitated in methanol (0.3 g). The crude product was dissolved in THF and precipitated in methanol. The dissolution-precipitation was repeated two times. Finally, the polymer was dried in a vacuum oven at 40 ^oC ($M_{n,theo}$ = 20880 g/mol (a sum of theoretical MWs of individual arms), $M_{n,NMR}$= 17135 g/mol, $M_{n,GPC}$ = 11150 g/mol, M_w/M_n = 1.29, relative to PS standards).

^{1}HNMR (500 MHz, $CDCl_3$, δ) 7.6-7.0 (m, 9H, C*H* of triazole and Ar*H*), 6.1 (bs, C=*H*, trans), 5.8 (bs, C=C*H*, cis), 5.5 (br, 2H, CH_2-Diels-Alder adduct), 5.2 (br, 2H, triazole-CH_2OC=O), 5.0 (bs, C*H*O, cis and C*H* of TEMPO), 4.7 (br, 1H, C*H* bridge head proton), 4.5 (bs, C*H*O, trans and C=OC*H*CH_3-triazole), 4.3-4.2 (br, 6H, CH_2OC=O and C=OOCH_2), 4.0 (bs, CH_2O of PCL), 3.6-3.2 (bs, OCH_2CH_2 of PEG C=OOCH_2CH_2N, C=OOCH_2CH_2N, N-CH_2, C*H*-C*H*, OCH_3 of PEG and C*H*-C*H* bridge-protons), 2.6-2.2 (br, 8H, OC=OCH_2CH_2C=OO), 2.2 (bs, C=OCH_2 of PCL), 2.0-0.5 (m, aliphatic protons of PCL and butyl).

4. RESULT AND DISCUSSION

As a general perspective, this thesis describes the design and synthesis of various macromolecular structures such as V-shaped graft copolymers by combination of C/LRP methods with click reactions which involve CuAAC, NRC and Diels-Alder.

4.1 Synthesis of Maleimide-Terminated PEG for Diels-Alder Chemistry

Furan and maleic anhydride were reacted in toluen at 80 ^{o}C, then the formed 4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione,1, (figure 4.1)**,** was utilized for the synthesis of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione,2, by adding the solution 2-amino ethanol in methanol into dispersion of 4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione in methanol (figure 4.1)

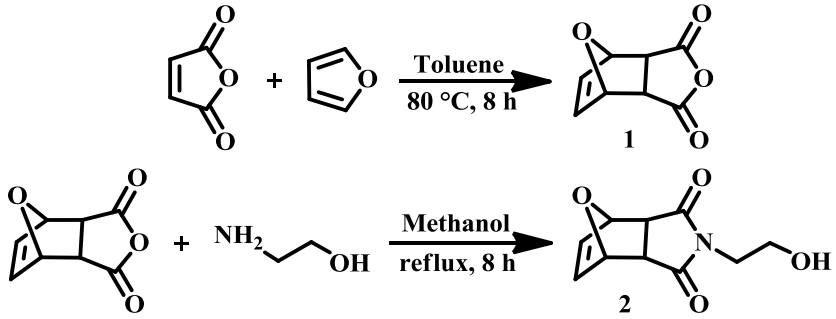
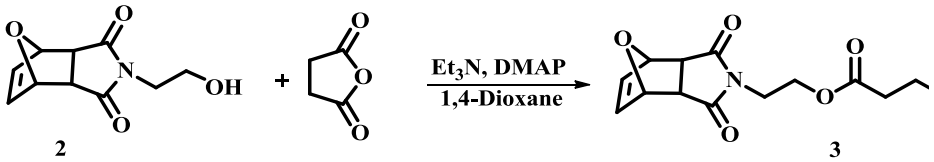


Figure 4.1: Synthesis of 1 and 2.

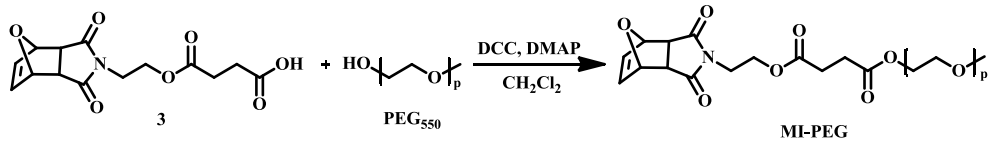
The hydoxyl functionality of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6] dec-8-ene-3,5-dione, 2, was converted to carboxylic acid via a reaction with succinic anhydride in the presence of Et_3N/DMAP catalyst system and 1,4-dioxane as solvent in order to give 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl)carbonyl]amino} ethoxy)-4-oxobutanoic acid**,** 3(Figure 4.2).



2 3

Figure 4.2: Synthesis of 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]heptyl)carbonyl] amino} ethoxy)-4-oxobutanoic acid.

MI-PEG was obtained as brown oil after esterification reaction between 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl)carbonyl]amino} ethoxy)-4-oxobutanoic acid and Me-PEG (550) (Figure 4.3). From ^{1}HNMR spectrum of the polymer, the bridge and bridge-head protons were detected at 6.5, 5.25 and 2.87 ppm respectively. The $M_{n,NMR}$= 750 of MI-PEG was determined from a ratio of integrated peaks at 3.62 ppm (OCH_2CH_2 protons of PEG) to 6.5 ppm (vinyl end protons), (Figure 4.3).



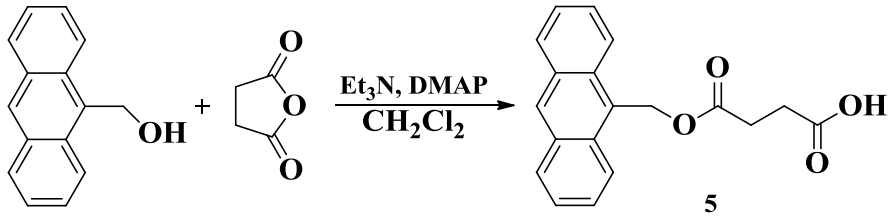
3 PEG550 MI-PEG

Figure 4.3: Synthesis of MI-PEG.

4.2 Synthesis of Trifunctional Linking Agent (Core) (10)

Anthraceno-9-ylmethyl-2-((2-bromo-2-methylpropanoyloxy)methyl)-2-methyl-3-oxo-3-(prop-2-ynyloxy)-propyl Succinate, 10, was synhesized within steps.

Succinic acid mono-anthracen-9-ylmethyl-ester, 5**,** synthesized by using 9-anthracene methanol as starting meterial (Figure 4.4).



5

Figure 4.4: Synthesis of Succinic acid mono-anthracen-9-ylmethyl-ester.

2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid, 7**,** was synthesized by is way; 2,2-bis (hydroxymethyl)-propanoic acid was reacted with excess amount of dry acetone using *p*-toluene sulfonic acid as catalyst. Additionally, 2,2-dimethoxy-propane was deliberately used to provide acetone during the reaction.

Then, propargyl alcohol was reacted with 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid, 6, in the presence of DCC/DMAP catalyst system and CH_2CL_2 as solvent in order to give propargyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate, **7**.

Next, propargyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate was dissolved in a mixture of THF and of HCl, then extracted with CH_2Cl_2 to give of propargyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate, 8.

Additionally, propargyl-3-[(2-bromo-2-methylpropanoyl)oxy-2-(hyroxymethyl)-2-methylpropanoate, 9, is synthesized by using 2-Bromo isobutrylbromide in the presence of CH_2Cl_2 solution system. Process is given below schematically (Figure 4.5).

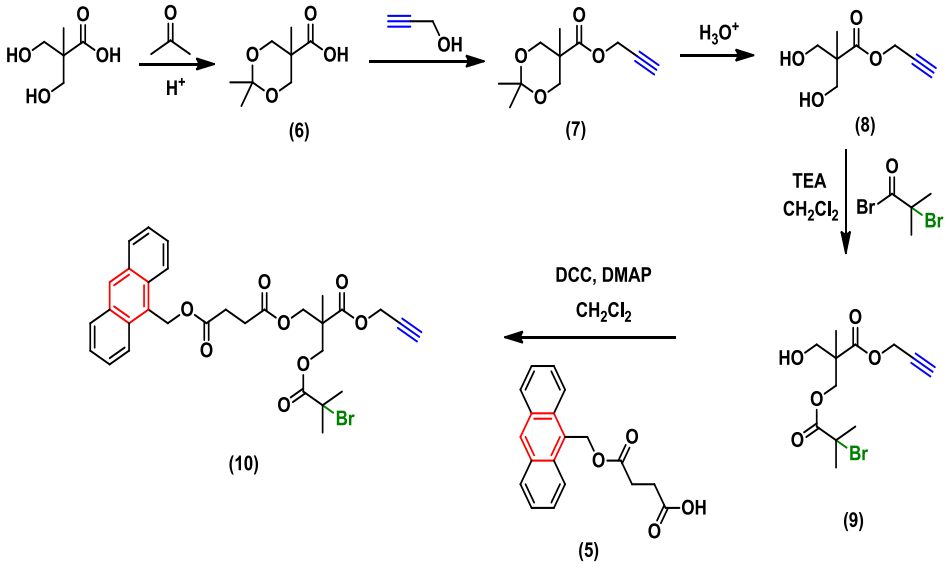


Figure 4.5: Synthesis of core

The ^{1}H NMR spectrum of the core shows the characterictic peaks that belongs to the three functions. As shown in Figure 4.6, the precence of the characteristic signals of anthracene protons resonating at 8.5-7.4 confirmed the antracene functionality. In addition, the acidic hydrogen of the terminal alkyne group is seen at 2.4 ppm.

4.3 Synthesis of Maleimide-Terminated PEG for Diels-Alder Chemistry

α-Alkyne-α-bromide-terminated PEG (PEG-alkyne/Br) is obtained via Diels-Alder click reaction of Propargyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate and 2-Bromo isobutrylbromide.

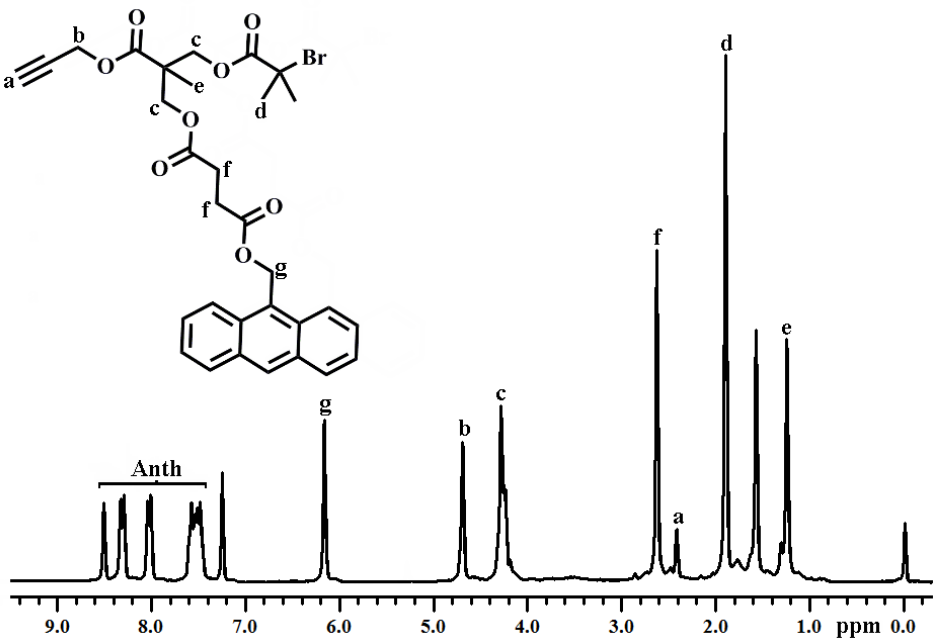


Figure 4.6: ^{1}H NMR spectrum of anhracen 9-methyl 2-2-((2-bromo-2-methyl prop anoyloxy)methyl)-2-methyl-3-oxo-3-(prop-2-ynyloxy)propylsuccinate,3 (500 MHz).

The PEG-MI ($M_{n,NMR}$ = 850 g/mol) was clicked with CORE through Diels-Alder click reaction to yield the PEG-alkyne/Br at 110 ^{o}C for 24 h in toluene. The chemical structure of PEG-alkyne/Br was verified by ^{1}H NMR spectroscopy.

As shown in Figure 4.7, the characteristic signals of anthracene protons resonating at 8.5-7.4 shifted to 7.4-7.1 ppm due to the disappearance of aromaticity in the central phenyl ring of anthracene, while confirming the Diels-Alder reaction of PEG-MI with core.

In addition, the presence of signals for the OCH_2CH_2 protons of PEG at 3.8-3.4 ppm confirmed the target structure.

4.4 Preparation of Backcone Copolymer of St and 4-chloromethylstyrene with Azide Pendant units, P(St_{48}-$Azide_5$)

To form the backbone polymers, St and CMS were polymerized via NMP at 125 ºC in order to give P(S-*co*-CMS) random copolymer using with a feed ratio of 10 mol % CMS (Figure 4.8). CMS value in the copolymer was calculated to have 9,4% by ^{1}H NMR.

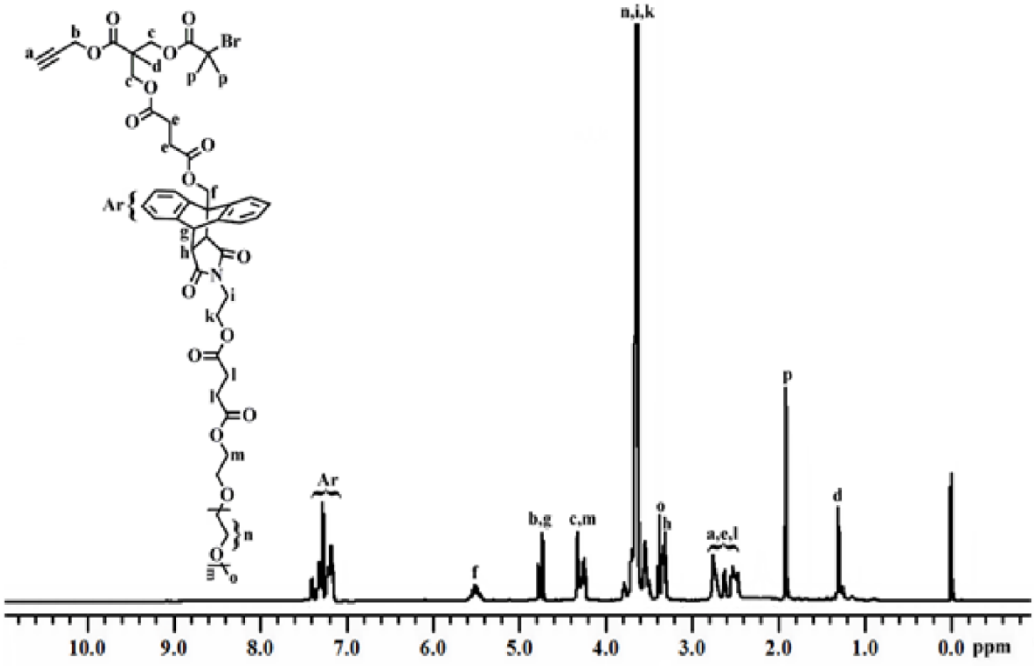


Figure 4.7: ^{1}H NMR α-alkyne-α-bromide-terminated PEG (PEG-alkyne/Br) via Diels-Alder click reaction of PEG-MI with 6 (500 MHz)

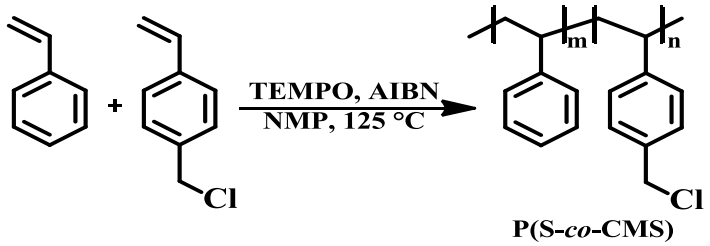


Figure 4.8: Preparation of P(St_{48}-$Azide_5$)

^{1}H NMR calculation from integrals of aromatic protons (δ 6.5-7.5) and CH_2Cl (δ 4.5) displayed 9,4 % of CMS, that the incorporations of CMS into the copolymer agree well with the feed ratios. Again, exploiting the $M_{n,GPC}$ values of copolymers, DP_n of St and CMS in these copolymers were calculated to have 48 and 5. (Figure 4.9).

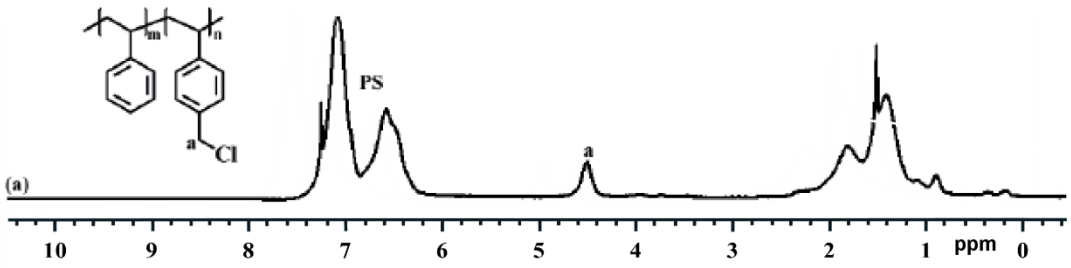


Figure 4.9: ^{1}H NMR of P(S-*co*-CMS) random copolymer (500 MHz).

Next, the copolymer was sequentially reacted with NaN_3 to give PS with azide pendant units. Number of azide pendant units calculated by ^1H NMR. The peak for Ph-C*H*$_2$Cl proton shift to 3.9 ppm as C*H*(Ph)-N_3 proton.

4.5 Synthesis of Backbone Copolymer with Azide Pendant Units, Poly(ONB-butyl)$_{15}$-*b*-Poly(ONB-Azide)$_5$

The first generation Grubbs' catalyst $(PCy_3)_2(Cl)_2$-RuCHPh is used to synthesize Poly(ONB-butyl)$_{15}$-*b*-Poly(ONB-Azide)$_5$ copolymer via ROMP of *N*-butyl oxanorbornene imide (ONB-butyl) and 2-bromo-propionicacid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl)-ethyl ester. The result copolymer is successfully obtained. Process is given below schematically.

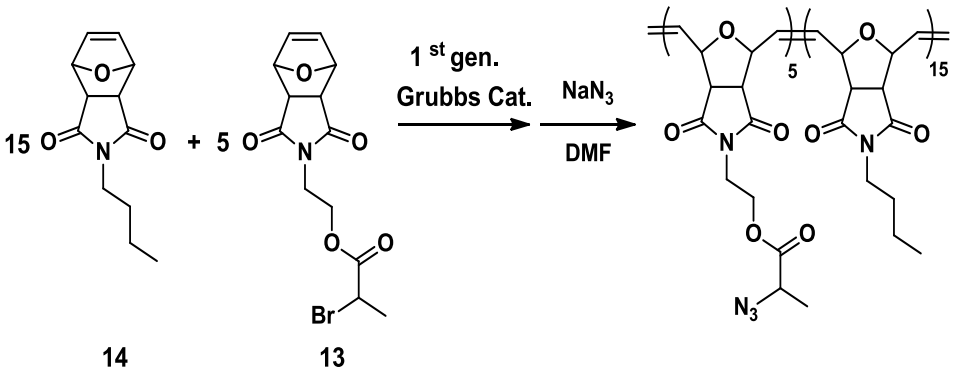


Figure 4.10: Preparation of Poly(ONB-butyl)$_{15}$-*b*-Poly(ONB-Azide)$_5$.

The characteristic peaks of the resulted backbone polymer, including bromine pendant units, are shown on ^1H NMR spectra as C=C*H*, trans proton at 6.1 ppm; C=C*H*, cis proton at 5.8 ppm; C*H*O, cis proton at 5.0 ppm; C*H*O, trans proton and C*H*Br proton at 4.5-4.3 ppm.

When bromine units turn into azide units the peak which was at 4.3 ppm turn into the peak C*H*N_3 at 3.8 ppm. This shows the conversion of bromine units to azide functionality. In additon, in FTIR spectra, 2113 cm^{-1} azide stretching is another proof of this conversion (Figure 4.11).

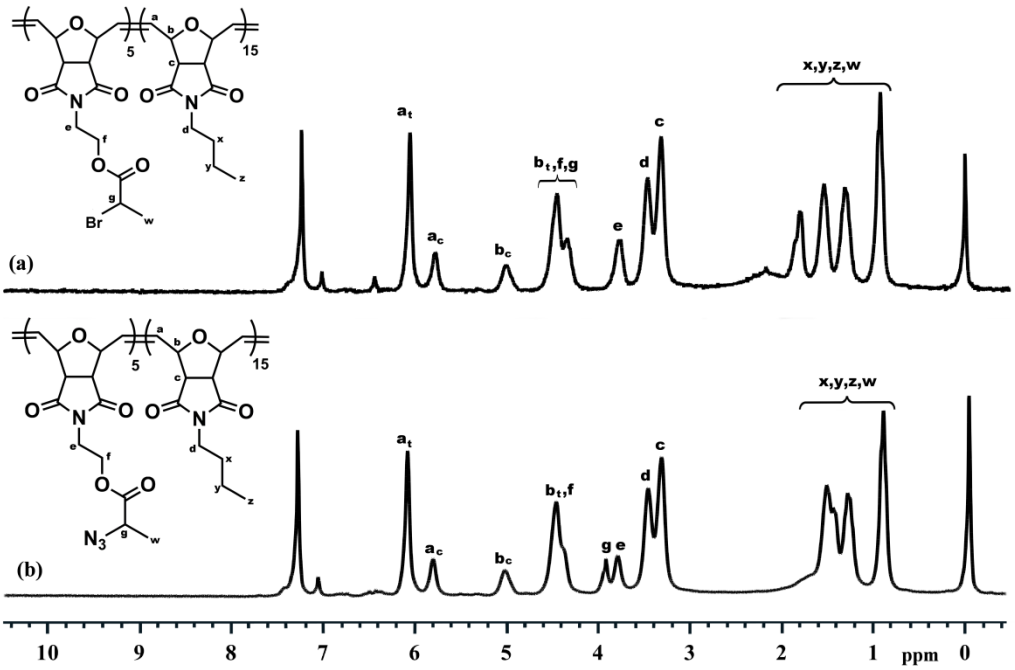


Figure 4.11: ^{1}H NMR datas of Poly(ONB-butyl)$_{15}$-*b*-Poly(ONB-Br)$_5$ and Poly(ONB-butyl)$_{15}$-*b*-Poly(ONB-Azide)$_5$ copolymers (500 MHz).

4.6 One-pot Synthesis of V-shaped P(St$_{48}$-Azide$_5$)-*g*-(PEG-PCL)

The CuAAC and NRC click reactions of PEG-alkyne/Br with P(St$_{48}$-Azide$_5$) and PCL-TEMPO respectively in a one pot fashion were conducted in DMF using Cu(0)/Cu(I) catalyst at room temperature for 12 h to afford an V-shaped polymer, P(St$_{48}$-Azide$_5$)-*g*-(PEG-PCL) (Figure 4.12).

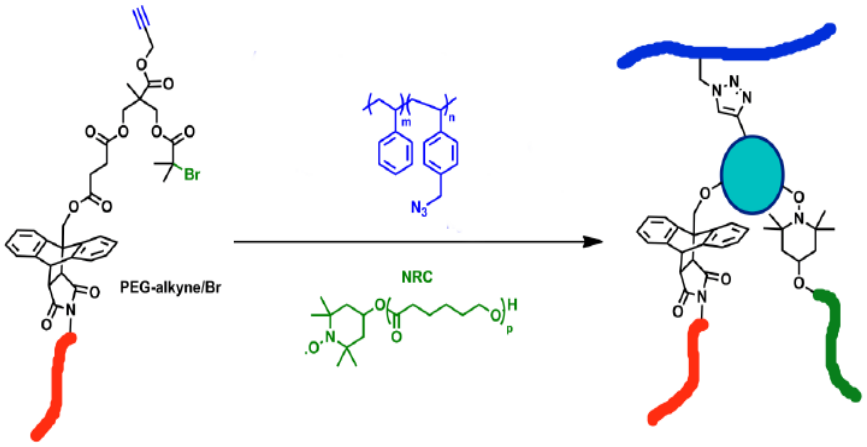


Figure 4.12: One-pot synthesis of V-shaped P(St$_{48}$-Azide$_5$)-*g*-(PEG-PCL).

As measured by ^{1}H NMR and GPC measurements, successful one-pot double click reactions had occurred. The ^{1}H NMR spectroscopy of the P(St_{48}-$Azide_5$)-*g*-(PEG-PCL) polymer indicated the appearance of the triazole CH proton at 7.6 ppm, along with the aromatic protons of PS at 7.3-6.2 ppm, the CH2O and C=OCH_2 protons of PCL at 4.0 and 2.2 ppm respectively, and the CH_2CH_2O protons of PEG at 3.6 ppm (Figure 4.13).

The NMR integral ratios of the PEG protons and the CH_2O protons of PCL versus aromatic protons of PS protons gave the DP_ns of the PEG and PCL segments to be 10 and 11 for each arm, which were in good agreement with those of the PEG and PCL precursors, 13 and 16, respectively assuming that the DP_n value of the PS segment in the V-shaped polymer was 53.

Therefore, $M_{n,NMR}$ was calculated to be (((10 X 44) + 290) g/mol X 5) + (11 X 114 g/mol X 5) + (53 X 104 g/mol) + (611 X 5 M of core) = 18850 g/mol, which was in close agreement with the theoretical molecular weight of 21480 g/mol (sum of the theoretical values of the precursors). The GPC analysis of the P(St_{48}-$Azide_5$)-*g*-(PEG-PCL) V-shaped polymer demonstrated a clear shift to a higher molecular weight region with respect to its related polymer precursors, while maintaining a monomodal molecular weight distribution.

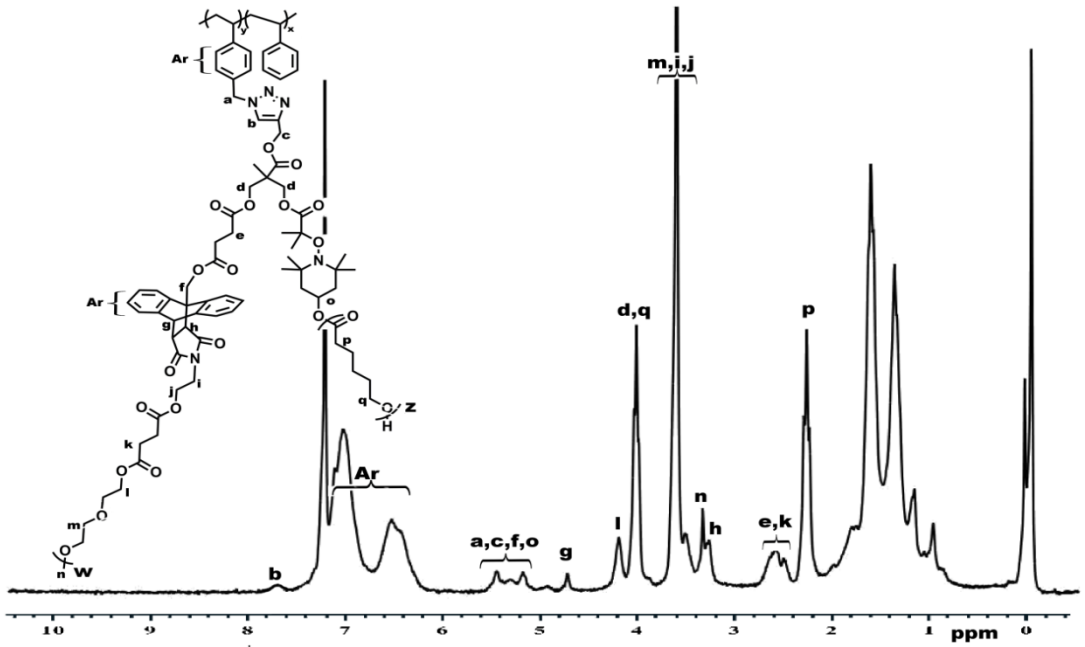


Figure 4.13: ^{1}H NMR of One-pot synthesis of V-shaped P(St_{48}-$Azide_5$)-*g*-(PEG-PCL) (500 MHz).

Evolution of GPC traces: *c*-PS, PEG-TEMPO and (*c*-PS)-*b*-PEG cm^{-1} azide stretching is another proof of this conversion (Figure 4.14).

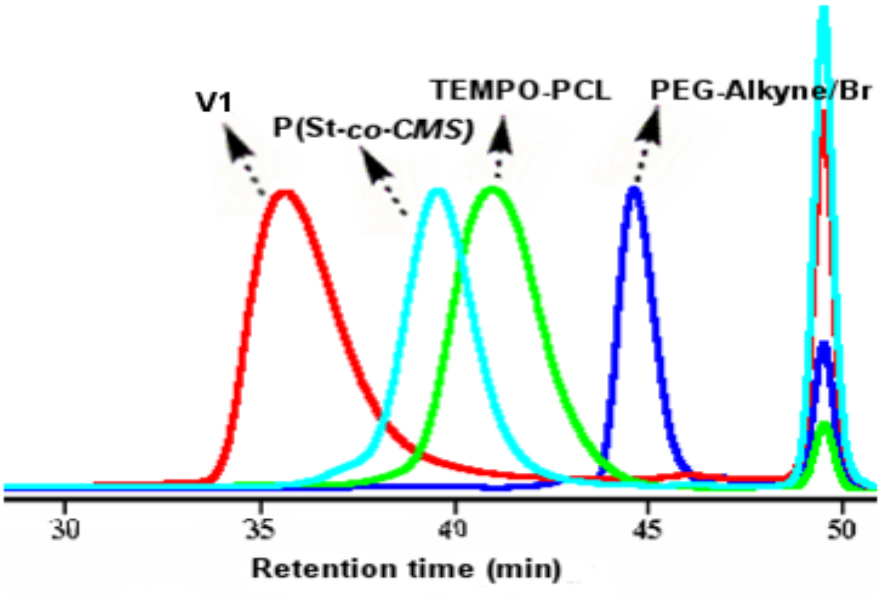


Figure 4.14: The evolution of GPC traces: V1, PCL-TEMPO, P(St-*co*-CMS) and PEG-Alkyne/Br.

4.7 One-pot Synthesis of V-shaped P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$)-*g*-(PEG-PCL)

CuAAC and NRC click reactions of PEG-alkyne/Br with P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$) and PCL-TEMPO respectively in a one pot fashion were conducted in DMF using Cu(0)/Cu(I) catalyst at room temperature for 12 h to afford an V-shaped polymer, P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$)-*g*-(PEG-PCL). As measured by ^{1}H NMR and GPC measurements, successful one-pot double click reactions had occurred (Figure 4.15).

The ^{1}H NMR spectroscopy of the P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$)-*g*-(PEG-PCL)) polymer indicated the appearance of the triazole CH proton at 7.6 ppm, along with the C=C*H*, trans proton at 6.1 ppm; C=C*H*, cis proton at 5.8 ppm; C*H*O, cis proton at 5.0 ppm; C*H*O, trans proton of the main backbone polymer, the CH_2O and $C{=}OCH_2$ protons of PCL at 4.0 and 2.2 ppm respectively, and the CH_2CH_2O protons of PEG at 3.6 ppm (figure 4.16).

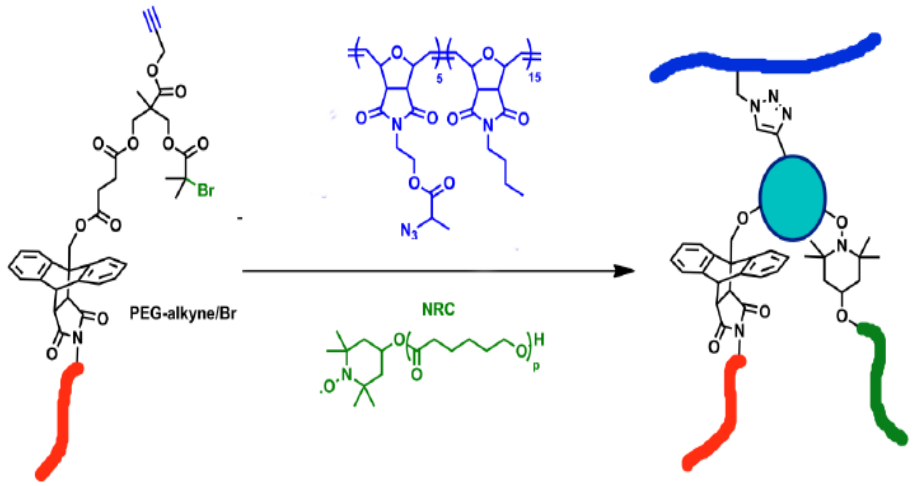


Figure 4.15: One-pot synthesis of V-shaped P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$)-*g*-(PEG-PCL).

The NMR integral ratios of the PEG protons and the C*H*$_2$O protons of PCL versus C=C*H*, trans proton of at 6.1 ppm of the main backbone gave the *DP*$_n$s of the PEG and PCL segments to be 11 and 10 for each arm, which were in good agreement with those of the PEG and PCL precursors, 13 and 16, respectively assuming that the *DP*$_n$ value of the main segment in the V-shaped polymer was 20. Therefore, $M_{n,NMR}$ was calculated to be (((10 X 44) + 290) g/mol X 5) + (11 X 114 g/mol X 5) + (53 X 104 g/mol) + (611 X 5 M of core) = 18850 g/mol, which was in close agreement with the theoretical molecular weight of 21480 g/mol (sum of the theoretical values of the precursors).

The GPC analysis of the P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$)-*g*-(PEG-PCL) V-shaped polymer demonstrated a clear shift to a higher molecular weight region with respect to its related polymer precursors, while maintaining a monomodal molecular weight distribution (Figure 4.17).

The dn/dc values of the V-shaped polymers were calculated by ^{1}H NMR spectroscopy depending on an assumption that dn/dc value is correlated linearly with composition of block copolymer. These calculated dn/dc values are subsequently introduced to the TD-GPC instrument, affording the $M_{w,TDGPC}$, $M_{n,TD,GPC}$, [η] and R_h of the analyzed miktoarm star polymers (Table 4.1). The $M_{n,TDGPC}$ of the P(St$_{48}$-Azide$_5$)-*g*-(PEG-PCL) and P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$)-*g*-(PEG-PCL) V-shaped polymers were in agreement with their corresponding $M_{n,theo}$ and $M_{n,NMR}$ values.

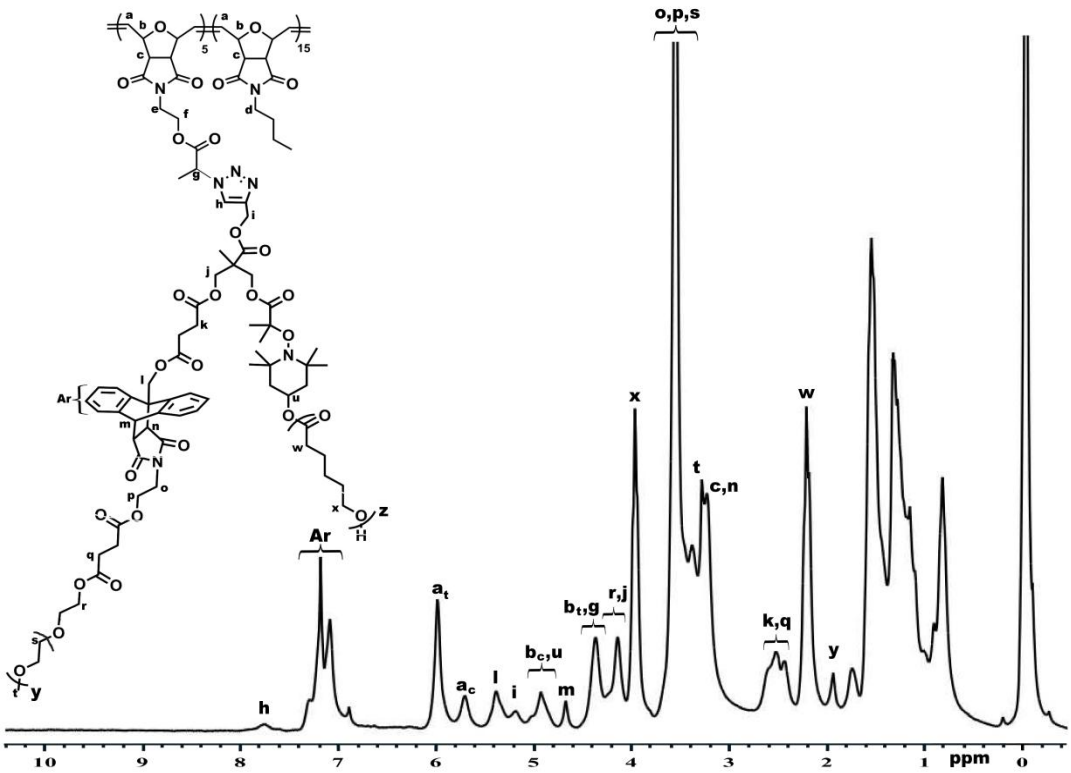


Figure 4.16: ^{1}H NMR One-pot synthesis of V-shaped P((ONB-butyl)$_{15}$-(ONB-Azide)$_5$)-*g*-(PEG-PCL) (500MHz).

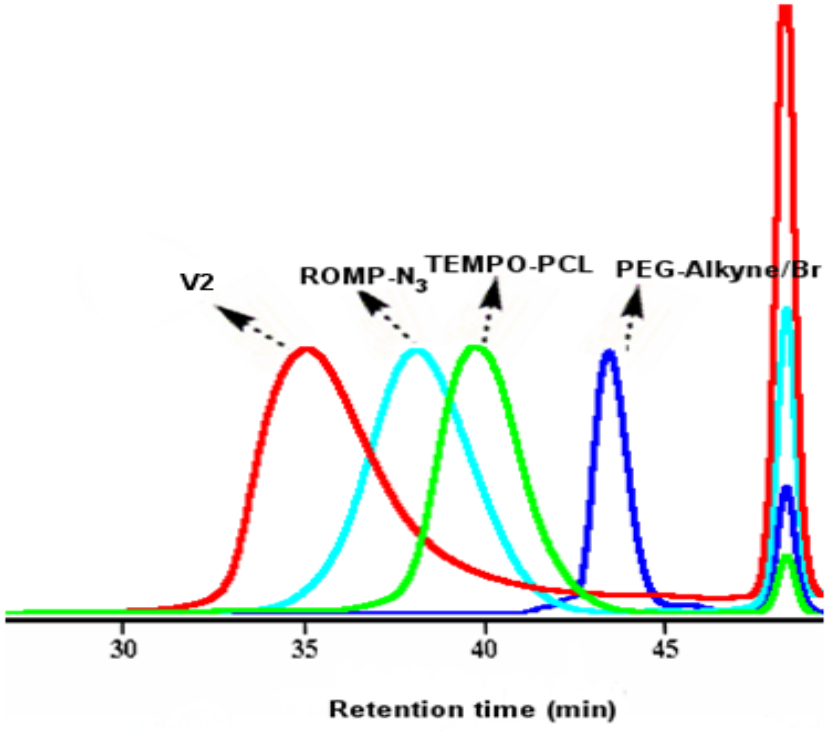


Figure 4.17: The evolution of GPC traces: V2, PCL-TEMPO, (ONB-butyl)$_{15}$-(ONB-Azide)$_5$ and PEG-Alkyne/Br.

Table 4.1 : GPC characterization of V-shaped graft copolymers.

Polymer	GPC[a]		TD-GPC[b]				
	M_n (g/mol)	M_w/M_n	M_n (g/mol)	M_w/M_n	R_h (nm)	$[\eta]$ (dL/g)	d*n*/dc (mL/g)
ST	14800	1.18	23150	1.27	4.04	0.15	0.115
ROMP	11150	1.29	22000	1.34	3.96	0.14	0.092

[a] Calculated using conventional GPC in THF at 30 ºC relative to PS standards;
[b]Calculated using triple detection GPC (TD-GPC) in THF at 35^{o}C.

5. CONCLUSION

As a general perspective, this thesis describes the design and synthesis of various macromolecular structures such as V-shaped graft copolymers by combination of C/LRP methods with click reactions which involve CuAAC, NRC and Diels-Alder.

Various backbone copolymers are synthesized and their characterizations are done by ^{1}H NMR datas. In addition, resulted copolymers are analyzed by ^{1}H NMR and GPC traces.

The GPC traces of the resulting V-shaped polymers exhibited a clear shift to higher molecular weight region relative to their precursors. It should be noted that the triple click reaction methodology employed here provides a simple and an efficient way to produce V-shaped graft copolymers with various compositions.

REFERENCES

[1] **Altintas, O.; Vogt, A. P.; Barner-Kowollik, C.; Tunca, U.,** 2012. Polymer Chemistry Review **DOI:** 10.1039/C1PY00249J.

[2] Hadjichristidis, N., Pispas, S., Pitsikalis, M., Iatrou, H., Lohse, D. J., 2004. *In Encyclopedia of Polymer Science and Technology, 3rd ed*.; Mark, H., Ed.; Wiley: New York, 2004; Vol. 6, pp 348–385.

[3]Velichkova, R. S., Christova, D. C., 1995, Amphiphilic polymers from macromonomers and telechelics, *Progress in Polymer Science*, **20,** 819-887.

[4] Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. Prog Polym Sci 2006, **31**, 1068–1132.

[5] Matyjaszewski, K. Prog Polym Sci 2005**, 30**, 858–875.

[6] Iatrou, H.; Mays, J. W.; Hadjichristidis, N. Macromolecules 1998, 31, 6697–6701.

[7] Ryu, S. W.; Asada, H.; Watanabe, T.; Hirao, A. Macromolecules 2004, **37**, 6291–6298.

[8] Xie, M. R.; Dang, J. Y.; Han, H. J.; Wang, W. Z.; Liu, J. W.; He, X. H.; Zhang, Y. Q. Macromolecules 2008, **41**, 9004–9010.

[9] Durmaz, H.; Dag, A.; Altintas, O.; Erdogan, T.; Hizal, G.; Tunca, U. Macromolecules 2007, **40**, 191–198.

[10] Stanford, M. J.; Dove, A. P. Macromolecules 2009, **42**, 141–147.

[11] Altintas, O.; Yankul, B.; Hizal, G.; Tunca, U. J. Polym. Sci., Polym. Chem. 2007, **45**, 3588–3598.

[12] Cheng, C.; Khoshdel, E.; Wooley, K. L. Macromolecules 2007, **40**, 2289–2292.

[13] Charvet, R.; Novak, B. M. Macromolecules 2004, **37**, 8808–8811.

[14]Ochiai, B.; Kato, Y.; Endo, T. Macromolecules 2009, **DOI:** 10.1021/ma901834d.

[15] Lutz, J. F. Angew. Chem., Int. Ed. 2007, **46**, 1018–1025.

[16] Lodge, T. P. Macromolecules 2009, **42**, 3827–3829.

[17] Luo, X. L.; Wang, G. W.; Pang, X. C.; Huang, J. L. Macromolecules 2008, **41**, 2315–2317.

[18] Parrish, B.; Breitenkamp, R. B.; Emrick, T. J. Am. Chem. Soc. 2005, **127**, 7404–7410.

[19] Zhang, Y.; He, H. K.; Gao, C. Macromolecules 2008, **41**, 9581–9594.

[20] Sumerlin, B. S.; Tsarevsky, N. V.; Louche, G.; Lee, R. Y.; Matyjaszewski, K. Macromolecules 2005, **38**, 7540–7545.

[21] Li, C. H.; Ge, Z. S.; Fang, J.; Liu, S. Y. Macromolecules 2009, **42**, 2916–2924.

[22] Ranjan, R.; Brittain, W. J. Macromolecules 2007, **40**, 6217–6223.

[23] Miyamoto, M., Sawamoto, M., and Higashimura, T., 1984. Living Polymerization of Isobutyl Vinyl Ether with the Hydrogen Iodide Iodine Initiating System, *Macromolecules*, **17,** 265-268.

[24] Szwarc, M., 1956. Block copolymers, *Nature*, **178**, 1168.

[25] Quirk, R. P.; Kinning, D. J.; Fetters, L. J., 1989. Comprehensive Polymer Science, Aggarwal, S. L.,Vol 7, p.1, Ed. Pergamon Press, London.

[26] Matyjaszewski, K., 1995. Introduction to Living Polymerization, Living and/or Controlled Polymerization, *J. Phys. Org. Chem.*, **8(4),** 197-207.

[27] Percec, V.; Tirrel, D. A., 2000. Living or Controlled ?, *J. Polym. Sci., Part A: Org. Ppoly Chem.*, **38(10),** 1705-1752.

[28] Quirk, R.; Lee, B., 1992. Terminology and classification of quasiliving polymerizations and ideal living polymerizations on the basis of the logic of elementary polymerization reactions, and comments on using the term controlled,.4. *Polym. Int.*, **27,** 359.

[29] Matyjaszewski, K.; Lin, C. H., 1991. Naming of controlled, living polymerizations, *Makromol. Chem. Macromolecules Symp.*, **47**, 221.

[30] Litvinienko, G.; Müler, A. H. E., 1997. General kinetic analysis and comparison of molecular weight distributions for various mechanisms of activity exchange in living polymerizations, *Macromolecules*, **30**, 1253.

[31] Wang, J.S.; Matyjaszewski, K., 1995, Controlled living radical polymerization - atom-transfer radical polymerization in the presence of transition-metal complexes, *Journal of the American Chemical Society*, **117,** 5614-5615.

[32] Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T., 1995, Polymerization of methyl-methacrylate with the carbon-tetrachloride dichlorotris (triphenylphosphine) ruthenium(ii) methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system - possibility of living radical polymerization, *Macromolecules*, **28,** 1721-1723.

[33] Georges, M.K.; Veregin, R.P.N.; Kazmaier, P.M.; Hamer, G.K., 1993, Narrow molecular-weight resins by a free-radical polymerization process, *Macromolecules*, **26,** 2987-2988.

[34] Chiefari, J.; Chong, Y.K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T.P.T.; Mayadunne, R.T.A.; Meijs, G.F.; Moad, C.L.; Moad, G., Rizzardo, E.; Thang, S.H., 1998, Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process, *Macromolecules*, **31,** 5559-5562.

[35] Kamigaito, M., Ando, T., and Sawamoto, M., 2001, Metal-catalyzed living radical polymerization, *Chemical Reviews*, 101, 3689-3745.

[36] Grimaud, T.; Matyjaszewski, K., 1997. Controlled/"Living" radical polymerization of methyl methacrylate by atom transfer radical polymerization, *Macromolecules*, **30**, 2216.

[37] Matyjaszewski, K. and Xia, J.H., 2001. Atom Transfer Radical Polymerization, *Chem. Rev.*, **101,** 2921-2990.

[38] Goto, A. and Fukuda, T., 1999. Determination of the Activation Rate Constants of Alkyl Halide Initiators for Atom Transfer Radical Polymerization, *Macromol. Rapid Commun.*, **20,** 633-636.

[39] Matyjaszewski, K., 1997. Mechanistic and Synthetic Aspects of Atom Transfer Radical Polymerization, *Journal of Macromolecular Science-Pure and Applied Chemistry*, **A34,** 1785-1801.

[40] Druliner, J.D., 1991. Living Radical Polymerization Involving Oxygen-Centered Species Attached to Propagating Chain Ends, *Macromolecules*, **24,** 6079-6082.

[41] De Leon-Saenz, E., Morales, G., Guerrero-Santos, R., and Gnanou, Y., 2000. New Insights into the Mechanism of 1,2-Bis(trimethylsilyloxy)-tetraphenylethane-Induced Free Radical Polymerization: Application to the Synthesis of Block and Graft Copolymers, *Macromol. Chem. Phys.*, **201,** 74-83.

[42] Yamada, B., Nobukane, Y., and Miura, Y., 1998. Radical Polymerization of Styrene Mediated by 1,3,5-Triphenylverdazyl, *Polym. Bull.*, **41,** 539-544.

[43] Steenbock, M., Klapper, M., and Mullen, K., 1998. Triazolinyl Radicals - New Additives for Controlled Radical Polymerization, *Macromol. Chem. Phys.*, **199,** 763-769.

[44] Puts, R.D. and Sogah, D.Y., 1996. Control of Living Free-Radical Polymerization by a New Chiral Nitroxide and Implications for the Polymerization Mechanism, *Macromolecules*, **29,** 3323-3325.

[45] Hawker, 1994. Molecular weight control by a "living" free-radical polymerization process, *C. J. J Am Chem Soc*, **116**, 11185.

[46] Nishimura, M., Kamigaito, M., and Sawamoto, M., 1999. Living-Radical Polymerization of Styrene with Transition-Metal Dithiocarbamate/AIBN Systems: Halogen-Free Living Processes, *Abstr. Pap. Am. Chem. Soc.*, **218,** 521-POLY.

[47] Chiefari, J., Chong, Y.K., Ercole, F., Krstina, J., Jeffery, J., Le, T.P.T., Mayadunne, R.T.A., Meijs, G.F., Moad, C.L., Moad, G., Rizzardo, E., and Thang, S.H., 1998, Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process, *Macromolecules*, 31, 5559-5562.

[48] Barner-Kowollik, C., 2008, Handbook of RAFT polymerization.

[49] Moad, G., Rizzardo, E., and Thang, S.H., 2006, Living radical polymerization by the RAFT process - A first update, *Australian Journal of Chemistry*, 59, 669-692.

[50] Moad, G., Rizzardo, E., and Thang, S.H., 2009, Living Radical Polymerization by the RAFT Process - A Second Update, *Australian Journal of Chemistry*, 62, 1402-1472.

[51] Arnal M.L., Balsamo V., Lopez C.F., Contreras J., Carillo M., Schmalz H., et. 2001. *Macromolecules*, 34:7973.

[52] Odian, G., 1991. In *Principles of polymerization*, John Wiley & Sons: New York.

[53] Bielawski, C. W.; Grubbs, R. H., 2007, Living ring-opening metathesis polymerization, *Progress in Polymer Science*, **32,** 1-29.

[54] Dragutan V.; Dragutan I.; Balaban A.T., 2006, "Nobel Prize 2005 in chemistry for the metathesis reaction", Awarded for the development of the metathesis reaction in organic synthesis**,** *Platinum Metals Review*, **50(1),** 35-37.

[55] Kolb, H.C.; Finn, M.G.; Sharpless, K.B., 2001, Click chemistry: Diverse chemical function from a few good reactions, *Angewandte Chemie-International Edition*, **40,** 2004-2021.

[56] Diels, O.; Alder, K., 1928, Synthesen in der hydroaromatischen Reihe, *Justus Liebig's Annalen der Chemie*, **460,** 98-122

[57] Corey, E.J., 2002, Catalytic enantioselective Diels-Alder reactions: Methods, mechanistic fundamentals, pathways, and applications, *Angewandte Chemie-International Edition*, **41,** 1650-1667.

[58] Diels, O.; Alder, K., 1926, Über die Ursachen der Azoesterreaktion, *Justus Liebig's Annalen der Chemie*, **450,** 237-254.

[59] Fringuelli, F.; Taticchi, A., 2002. *The Diels Alder reaction : selected practical methods*. Chichester, New York, Wiley.

[60] Woodward, R.B.; Hoffmann, R., 1970. *The conservation of orbital symmetry*. Weinheim/Bergstr, Verlag Chemie.

[61] Woodward, R.B.; Hoffmann, R., 1965, Stereochemistry of electrocyclic reactions, *Journal of the American Chemical Society*, **87,** 395-397.

[62] Huisgen, R., 1963, 1.3-Dipolare cycloadditionen - ruckschau und ausblick, *Angewandte Chemie-International Edition*, **75,** 604-637.

[63] Padwa, A., 1984. *1,3-dipolar cycloaddition chemistry*. General heterocyclic chemistry series. New York, Wiley.

[64] Huisgen, R., 1968, On mechanism of 1,3-dipolar cycloadditions . Areply, *Journal of Organic Chemistry*, **33,** 2291-2297.

[65] Gothelf, K.V. and Jorgensen, K.A., 1998, Asymmetric 1,3-dipolar cycloaddition reactions, *Chemical Reviews*, **98,** 863-909.

[66] Rostovtsev, V.V., Green, L.G., Fokin, V.V., and Sharpless, K.B., 2002, A stepwise Huisgen cycloaddition process: Copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes, *Angewandte Chemie-International Edition*, **41,** 2596-2599.

[67] Tornoe, C.W., Christensen, C., and Meldal, M., 2002, Peptidotriazoles on solid phase: [1,2,3]-triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides, *Journal of Organic Chemistry*, **67,** 3057-3064.

[68] Appukkuttan, P., Dehaen, W., Fokin, V.V., and Van der Eycken, E., 2004, A microwave-assisted click chemistry synthesis of 1,4-disubstituted 1,2,3-triazoles.

[69] Fu, Q.; Wang, G.; Lin, W.; Huang, J., 2009. J. Polym. Sci., Part A: Polym. Chem., 47, (3), 986–990.

[70] Luo, X.; Wang, G.; Huang, J., 2008. J. Polym. Sci., Part A: Polym. Chem., 47, (1), 59–68.

[71] Fu, Q.; Liu, C.; Lin, W.; Huang, J., 2008. J. Polym. Sci., Part A: Polym. Chem., 46, (20), 6770–6779.

[72] Liu, C.; Pan, M.; Zhang, Y.; Huang, J., 2008. J. Polym. Sci., Part A: Polym. Chem., 46, (20), 6754–6761.

[73] Lin, W.; Fu, Q.; Zhang, Y.; Huang, J., 2008. Macromolecules, 41 (12), 4127–4135.

[74] Fu, Q.; Lin, W.; Huang, J., 2008. Macromolecules, 41 (7), 2381–2387.

[75] Nicolay, R.; Marx, L.; Hemery, P.; Matyjaszewski, K., 2007. Macromolecules, 40, (26), 9217–9223.

[76] Matyjaszewski, K.; Woodworth, B. E.; Zhang, X.; Gaynor, S. G.; Metzner, Z., 1998. Macromolecules, 31, 5955–5957.

[77] (a) Sun, R. M.; Wang, G. W.; Liu, C.; Huang, J. L., 2009. J Polym Sci Part A: Polym Chem, 47, 1930–1938; (b) Fu, Q.; Liu, C.; Lin, W. C.; Huang, J. L. J Polym Sci Part A: Polym Chem 2008, **46**, 6770–6779.

[78] (a) Fu, Q.; Wang, G. W.; Lin, W. C.; Huang, J. L., 2009 J Polym Sci Part A: Polym Chem, 47, 986–990; (b) **Liu, C.; Pan, M. G.; Zhang, Y.; Huang, J. L**., 2008. J Polym Sci Part A: Polym Chem**, 46**, 6754–6761.

[79] Lin, W. C.; Fu, Q.; Zhang, Y.; Huang, J. L., 2008. Macromolecules, 41, 4127–4135.

[80] Otsuka, H.; Aotani, K.; Higaki, Y.; Takahara, A., 2002.Chem. Commun., 2838–2839.

[81] Otsuka, H.; Aotani, K.; Higaki, Y.; Takahara, A. J.,2003. Am. Chem. Soc., 125, 4064–4065.

[82] Higaki, Y.; Otsuka, H.; Takahara, A.,2004. Macromolecules, 37, 1696–1701.

[83] Gao, C.; Yan, D., 2004. Hyperbranched polymers: From synthesis to applications. *Progress in Polymer Science* 29, (3), 183-275.

[84] Wang, C. C.; Guo, Z. X.; Fu, S. K.; Wu, W.; Zhu, D. B., 2004. Polymers containing fullerene or carbon nanotube structures. *Progress in Polymer Science* 29, (11), 1079-1141.

[85] Hadjichristidis, N., 2003. Polymer chemists/polymer physicists: A constructive partnership. *European Physical Journal E* 10, (1), 83-86.

[86] Davis, K. A.; Matyjaszewski, K., 2002. Statistical, gradient, block, and graft copolymers by controlled/living radical polymerizations. *Advances in Polymer Science* 159, 1-169.

[87] Mori, H.; Muller, A. H. E., 2003. New polymeric architectures with (meth)acrylic acid segments. *Progress in Polymer Science* 28, (10), 1403-1439.

[88] Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. Chem Rev 2001, **101**, 3747–3792.

[89] Quirk, R. P.; Yoo, T.; Lee, Y.; Kim, J.; Lee, B. Adv Polym Sci 2000, **153**, 67–162.

[90] Hadjichristidis, N.; Pitsikalis, M.; Iatrou, H.; Pispas, S. Macromol Rapid Commun 2003, **24**, 979–1013.

[91] Hadjichristidis, N.; Pispas, S.; Pitsikalis, M.; Iatrou, H.; Vlahos, C. Adv Polym Sci 1999, **142**, 71–127.

[92] Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Adv Polym Sci* 1998, **135**, 1–137.

[93] Hirao, A.; Hayashi, M.; Loykulnant, S.; Sugiyama, K. *Prog Polym Sci* 2005, **30**, 111–182.

[94] Hirao, A.; Sugiyama, K.; Tsunoda, Y.; Matsuo, A.; Watanabe, T. *J Polym Sci Part A: Polym Chem*, 2006, **44**, 6659–6687.

[95] Al-Muallem, H. A.; Knauss, D. M. *J Polym Sci Part A: Polym Chem* 2001, **39**, 152–161.

[96] Knauss, D. M.; Al-Muallem, H. A.; Huang, T. Z.; Wu, D. T. *Macromolecules* 2000, **33**, 3557–3568.

[97] Knauss, D. M.; Al-Muallem, H. A. *J Polym Sci Part A: Polym Chem* 2000, **38**, 4289–4298.

[98] Hirao, A.; Inoue, K.; Higashihara, T. *Macromol Symp* 2006, **240**, 31–40.

[99] Zhao, Y. L.; Higashihara, T.; Sugiyama, K.; Hirao, A. *J Am Chem Soc* 2005, **127**, 14158–14159.

[100] Higashihara, T.; Nagura, M.; Inoue, K.; Haraguchi, N.; Hirao, A., *Macromolecules* 2005, **38**, 4577–4587.

[101] Li, J. M.; Gauthier, M. *Macromolecules* 2001, **34**, 8918–8924.

[102] Orfanou, K.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *Macromolecules* 2006, **39**, 4361–4365.

[103] Chalari, I.; Hadjichristidis, N. *J Polym Sci Part A: Polym Chem* 2002, **40**, 1519–1526.

[104] Watanabe, T.; Tsunoda, Y.; Matsuo, A.; Sugiyama, K.; Hirao, A. *Macromol Symp* 2006, **240**, 23–30.

[105] Hirao, A.; Matsuo, A.; Watanabe, T. *Macromolecules* 2005, **38**, 8701–8711.

[106] Matsuo, A.; Watanabe, T.; Hirao, A. *Macromolecules* 2004, **37**, 6283–6290.

[107] Li, J. M.; Gauthier, M.; Teertstra, S. J.; Xu, H.; Sheiko, S. S. *Macromolecules* 2004, 37, 795–802.

[108] Ryu, S. W.; Hirao, A. *Macromol Chem Phys* 2001, **202**, 1727–1736.

[109] Vazaios, A.; Hadjichristidis, N. *J Polym Sci PartA: Polym Chem* 2005, **43**, 1038–1048.

[110] Pantazis, D.; Chalari, I.; Hadjichristidis, N. *Macromolecules* 2003, **36**, 3783–3785.

[111] Pitsikalis, M.; Sioula, S.; Pispas, S.; Hadjichristidis, N.; Cook, D. C.; Li, J. B.; Mays, J. W. *J Polym Sci Part A: Polym Chem* 1999, **37**, 4337–4350.

[112] Tsoukatos, T.; Pispas, S.; Hajichristidis, N. *Macromolecules* 2000, **33**, 9504–9511.

[113] Vazaios, A.; Lohse, D. J.; Hadjichristidis, N. *Macromolecules* 2005, **38**, 5468-5474.

[114] Koutalas, G.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *Macromolecules* 2005, **38**, 4996–5001.

[115] Koutalas, G.; Lohse, D. J.; Hadjichristidis, N.*J Polym Sci Part A: Polym Chem* 2005, **43**, 4040–4049.

[116] Christodoulou, S.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *J Polym Sci Part A: Polym Chem* 2005, **43**, 4030–4039.

[117] Driva, P.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *J Polym Sci Part A: Polym Chem* 2005, **43**, 4070–4078.

[118] Hirao, A.; Ryu, S. W. *Macromol Symp* 2003, **192**, 31–42.

[119] Iatrou, H.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* 1998, **31**, 6697–6701.

[120] Mays, J. W.; Uhrig, D.; Gido, S.; Zhu, Y. Q.; Weidisch, R.; Iatrou, H.; Hadjichristidis, N.; Hong, K.; Beyer, F.; Lach, R.; Buschnakowski, M. *Macromol Symp* 2004, **215**, 111–126.

[121] Xenidou, M.; Hadjichristidis, N. *Macromolecules* 1998, **31**, 5690–5694.

[122] Ryu, S. W.; Asada, H.; Watanabe, T.; Hirao, A. *Macromolecules* 2004, **37**, 6291–6298.

[123] Hirao, A.; Kawano, H.; Ryu, S. W. *Polym Adv Technol* 2002, **13**, 275–284.

[124] Yu, F.; He, J.; Wang, X.; Gao, G.; Yang, Y. *Journal of Polymer Science: Part A: Polymer Chemistry*, 2007,4013-4025, **DOI 10.1002/pola:22155**.

[125] Driva, P.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *J Polym Sci Pol Chem* 2005, **43**, 4070–4078.

[126] Gu, L. N.; Shen, Z.; Zhang, S.; Lu, G. L.; Zhang, X. H.; Huang, X. Y. *Macromolecules* 2007, **40**, 4486–4493.

[127] Xu, J.; Zubarev, E. R. *Angew Chem Int Ed* 2004, **43**, 5491–5496.

[128] Genson, K. L.; Holzmueller, J.; Jiang, C.; Xu, J.; Gibson, J. D.; Zubarev, E. R.; Tsukruk, V. V. *Langmuir* 2006, **22**, 7011–7015.

[129] Teng, J.; Zubarev, E. R. *J Am Chem Soc* 2003, **125**, 11840–11841.

[130] Zubarev, E. R.; Xu, J.; Sayyad, A.; Gibson, J. D. *J Am Chem Soc* 2006, **128**, 4958–4959.

[131] Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, **101**, 2921–2990.

[132] Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem Rev* 2001, **101**, 3661–3688.

[133] Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, **31**, 5559–5562.

[134] Percec, V.; Barboiu, B.; Bera, T. K.; van der Sluis, M.; Grubbs, R. B.; Jean, M. J.; Frechet, J. M. *J Polym Sci Pol Chem* 2000, **38**, 4776–4791.

[135] Percec, V.; Barboiu, B. *Macromolecules* 1995, **28**, 7970–7972.

[136] Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. *J Am Chem Soc* 2006**, 128**, 14156–14165.

[137] Percec, V.; Barboiu, B.; Grigoras, C.; Bera, T. K. *J Am Chem Soc* 2003, **125**, 6503–6516.

[138] Binder, W. H.; Sachsenhofer, R. *Macromol Rapid Commun* 2007, **28**, 15–54.

[139] Wang, G.; Liu, C.; Pan, M.; Huang, J. *Journal of Polymer Science: Part A: Polymer Chemistry*, 2008, 1308-1316 **DOI 10.1002/pola:22155**.

[140] Mantovani, G., Lecolley, F., Tao, L., Haddleton, D.M., Clerx, J., Cornelissen, J.J.L.M., and Velonia, K., 2005, Design and synthesis of N-maleimido-functionalized hydrophilic polymers via copper-mediated living radical polymerization: A suitable alternative to PEGylation **chemistry, *Journal of the American Chemical Society*, 127, 2966-2973**.

[141] Gacal, B.; Durmaz, H.; Tasdelen, M. A.; Hizal, G.; Tunca, U. ; Yagci, Y.; Demirel, A. L. *Macromolecules* 2006, **39**, 5330-5336.

[142] Lei, X.G. and Porco, J.A., 2004, Synthesis of a polymer-supported anthracene and its application as a dienophile scavenger, *Organic Letters*, **6,** 795-798.

[143] Gungor, E.; Durmaz, H.; Hizal, G.; Tunca, U. *J Polym Sci Part A: Polym Chem Ed* 2008, **46**, 4459–4468.

[144] Dag A; Durmaz, H.; Hizal, G.; Tunca,U. , Preparation of 3-Arm Star Polymers (A3) via Diels-Alder Click Reaction, *J. Polym Sci, Part A Poly. Chem. Ed.*, ,2008, **46**, 302-313.

[145] Durmaz, H.; Hizal, G.; Tunca, U. *J Polym Sci Part A: Polym Chem* 2011, **49**, 1962-1968.

[146] Runge, B.M.; Bowden, B.N., Synthesis of High Molecular Weight Comb Block Copolymers and Their Assembly into Ordered Morphologies in the Solid State, *J. AM. CHEM. SOC.* 2007, **129**, 10551-10560.

[147] Al-Badri, M.Z.; Tew, G.N., Well-Defined Acetylene-Functionalized Oxanorbornene Polymers and Block Copolymers, *Macromolecules* 2008, ***41,*** 4173-4179.

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PUBLICATIONS/PRESENTATIONS ON THE THESIS

1. Bengü ÖZSOY, Hakan DURMAZ, Ufuk Saim GÜNAY, Gürkan HIZAL, Ümit TUNCA Synthesis of v-Shaped Graft Copolymers via Triple Click Reactions *Eupoc 2012 International Congress – Europolymer Conference 2012,* 3-7 June 2012-Gargnano / Italy